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TECHNICAL AND ECONOMIC ASSESSMENT OF THE APPLICATION OF MEMBRANE TECHNOLOGY FOR TREATING OIL/WATER/MINERAL EMULSIONS

FINAL REPORT

VOLUME II - EXPERIMENTAL WORK AND ECONOMIC ASSESSMENTS

Report Prepared for

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SUMMARY

The prime objective of this study was to assess the technical and economic viability of applying membrane technology to the treatment of produced water emulsions.

A review of literature and present technology suggested that there is considerable potential for membrane application to produced water treatment. Ultrafiltration membranes have been used successfully in other industries for emulsified oil recovery and reverse osmosis systems have been successfully applied to the treatment of boiler feedwater.

Initial laboratory work involved a complete characterization of a sample of produced water emulsion. The concentration of oil in a very stable emulsion was 1700 mg/L. GC analysis showed the presence of 60 mg/L of naphthenic acid which is thought to contribute to the high stability of the emulsion.

Prescreening tests were conducted on twenty membranes manufactured from 6 different materials. One membrane of each type of material was chosen for further work based on the results of prescreening tests.

Membrane screening tests with the six best membranes were conducted at 25°C and 45°C with the pH of the feed adjusted to 5.5, left "as is" near 7.5, and adjusted to 9.5 and at 65°C with the pH left "as is". These tests showed clearly that flux rates increase at increasing temperatures and that higher pH appears to favour better flux rates. All membranes consistently removed virtually all oil from the feed. The TFC G10 membrane rejected the highest percentage of all

contaminants and maintained very stable flux rates during the tests. Membranes CHP Cat and PS E500 had generally higher flux rates than the TFC membrane but showed some decline of flux during the tests. Other membranes either had poor quality permeate or lower flux rates.

A batch concentration (to a 90% volume reduction) test and a long term stability test demonstrated that flux rates could be relatively high even at high volume reductions (0.62 m^3/m^2D at 80% volume reduction). The results also demonstrated that effective cleaning procedures will be critical to the economic viability of the application. Reverse osmosis tests demonstrated that RO membranes can in one simple step produce boiler feed water quality water from produced water which has had oil removed.

Economic assessments were conducted for UF/Sodium Zeolite softening, UF/RO, and induced gas floatation/filtration/RO processes for produced water treatment. The costs per thousand gallons treated, including capital amortization and operating costs were $4.84, $6.95, and $7.06 respectively. The costs for tubular UF systems were prohibitive at the flux rates assessed in this study but may prove to be economical if flux rate improvements with tubular systems can be realized.

Further work should focus on assessing operation of configured membrane systems for potential flux rates and cleanability of such configured and larger scale systems. Higher temperature operation should also be explored as well as field testing to assess the impact of emulsion aging.

1.0 INTRODUCTION

This report by ZENON Environmental is submitted to CANMET division of the Department of Energy, Mines, and Resources, Canada in partial fulfillment of the requirements of the Contract, "Technical and Economic Assessment of the Application of Membrane Technology for Treating Oil/Water/Mineral Emulsions".

Volume I of this report contains a review of literature and industrial processes related to this topic. This volume (Volume II), contains the results of experimental work conducted by ZENON Environmental. Ultrafiltration (UF) membranes were evaluated in a small membrane test unit at different temperatures and pH. Selected membranes were tested in the small test unit at a ten fold concentration of the feed, over an extended period of time. Reverse osmosis membranes were also evaluated in a small test unit using permeate from the UF system and chemically demulsified produced water. This volume also contains the results of an economic assessment estimating the capital and operating costs for different processes treating produced water emulsions. These estimates are based on the results of experimental work, ZENON's in-house membrane system manufacturing experience, and contacts with suppliers of other process components.

The Appendices to this report are presented in Volume III.

2.0 EXPERIMENTAL PROCEDURES

2.1 Sample Characterization

2.1.1 Sample Description

Ten 45 gallon drums of wellhead emulsion were obtained from Texaco Canada's in-situ heavy oil recovery operation at Fort McMurry, Alberta. The drums each contained a layer of settled heavy oil sludge, a layer of light surface oil, and middle layer containing a stable oil in water emulsion. This oil in water emulsion represented approximately 90% by volume of the samples obtained. The surface oil layers from each of the drums were skimmed off and the emulsion layers were pumped into a large stainless steel mixing tank. This composite emulsion was mixed for several hours then transferred to clean 45 gallon drums for use throughout the experiments. Prior to samples being taken from a drum the contents were mixed to insure that a representative sample was being obtained. The composite emulsion, free of surface oil and settled sludge, was considered to be roughly equivalent to the effluent of a skim tank used in oil field operations. The removal of suspended oil in this manner is not difficult to carry out as a pretreatment for large-scale operation and can be expected to significantly improve membrane system operation.

In order to evaluate the variability of produced water three additional one liter samples of wellhead emulsion containing higher oil contents were also obtained from Texaco's Fort McMurry operation. These samples had been collected at the Fort McMurry pilot plant over a six month period in the latter half of 1983. The oil in water emulsions from these three samples were separated from the light surface oil layers and the settled heavy oils.

2.1.2 Particle Size Analysis

Physical characterization of the emulsion was conducted because of the importance of particle size in emulsion stability and membrane system operation.

Particle size distribution measurements were conducted by the Ontario Research Foundation on an unfiltered sample of the emulsion. A 1 mL portion of raw sample was also washed with 50 mL of toluene in a separatory funnel. To this, 9 mL of Isoton (a particle free aqueous electrolyte) was added to aid in particle dispersion and separation. Once the oil had been removed from the aqueous phase (as noted by a change in color of both the toluene and aqueous layers), the aqueous portion was collected for particle size analysis. Residual clay particles in the separatory funnel were washed through and collected with successive additions of Isoton.

Particle size measurement on both the raw sample and the toluene washed sample were conducted on a Coulter Counter TAII using a 70 micron aperture tube which provided an effective size range of 1.6 - 32+ micron. By preparing accurately diluted samples and metering a precise sample volume through the aperture tube, estimates of particle concentraton, within the range stated above, could be deduced. To arrive at the size distribution for the oil droplets, the toluene washed sample data (e.g. clay particles) were subtracted from the total or raw sample.

2.1.3 Emulsion Stability

The stability of the large volume sample of produced water emulsion was evaluated by examining the effect of pH, heating,

freezing, and demulsifier addition on emulsion stability. The stability of the three higher oil content samples with respect to pH was also evaluated. These simple tests were conducted to provide background information on the technical feasibility of alternative processes for emulsion separation.

Effect of pH

In order to determine the stability of the emulsions with respect to pH, samples were pH adjusted to different values with NaOH or H_2SO_4.

The pH of 50 mL samples of the large volume of "typical" emulsion were adjusted to values of 2, 4, 4.5, 5.0, 5.5, 6, 8, 10, and 12. The samples were mixed and allowed to stand for several hours. The degree of separation over time and quality of supernatant were observed and recorded. Samples of the higher oil content emulsion had their pH adjusted to 3.0, 3.5 and 4.0. Again the effects on emulsion stability were observed.

Effect of Freezing

A 100 mL sample of emulsion was placed in a polyethelene container and put in a freezer for 24 hours. The container was removed from the freezer and allowed to warm to room temperature. The degree of separation and quality of supernatant obtained were observed.

Effect of Heating

An aliquot of emulsion was heated in a boiling water bath for a 1/2 hour period of time. The sample was then allowed to cool and the degree of separation and quality of supernatant obtained were observed.

Effects of Chemical Demulsifiers

Four samples of chemical demuslifiers were obtained from Witco Chemical. The four demulsifiers obtained were RTC 323, RTC 326, RTC 327, and RTC 330. General information on Witco's reverse demulsifiers and typical properties for RTC-323 are presented in Appendix A. These products are specified for breaking stable oil in water emulsions and are referred to by Witco as reverse demulsifiers. For the purpose of this report they will be referred to simply as demulsifiers.

Stock dilutions containing 10% by volume of each demulsifier were prepared with tap water and with a 2% ZnCl solution. One mL portions of each of the eight solutions were added to beakers containing 100 mL of produced water emulsion. The contents of the beakers were mixed and then allowed to stand. The degree of separation with time and quality of the supernatant were observed and recorded. The solutions which were successful in breaking the emulsion at a 10% concentration level were further diluted to 2.5% and 0.625% demulsifier in water or $ZnCl_2$ solution. The ability of these further diluted demulsifiers to break the emulsion was tested in the same manner as before.

2.1.4 Routine Chemical Analysis

The following analyses were conducted on the standard sample of emulsion at the start of experimental work and before the batch concentration tests:

pH,

Turbidity,

Conductivity,

Total Organic Carbon (TOC),

Filtered Organic Carbon (FOC),

Total Suspended Solids (TSS),

Total Suspended Oil (TSO),

Total Dissolved Solids (TDS),

Total Dissolved Oil (TDO),

Anions,

Cations,

Hardness (by calculation),

Dissolved Silica, and

Oil and Grease.

Initial analysis of the standard emulsion also included ethyl acetate extractable surfactant material as suggested by the scientific authority. The FOC, anion scan, cation scan, hardness, and silica measurements were done on samples which had been filtered prior to analysis. The procedures used for these analyses are presented in Appendix A.

These same analyses with the exception of oil and grease were performed on the three higher oil content emulsion samples.

2.1.5 GC and IR Analysis

Samples of the typical emulsion were prepared in three different ways for analysis by gas chromatography (GC) with a flame ionization detector (FID) and by infra-red spectrophotometry (IR). One hundred and fifty millilitres of the first sample was adjusted to pH 2 with concentrated hydrochloric acid and was then extracted with 50 mL of dichloromethane three times. The 150 mL of organic extract was then evaporated down to a volume of 10 mL and dried by passing it through a bed of Na_2SO_4. A portion of the sample was then injected into a Hewlett-Packard 5880A gas chromatograph with flame ionization detection. A separate portion of this sample was subjected to analysis with a Beckman infra-red spectrophotometer. Details of the GC and IR conditions are presented in Appendix B.

The pH of the second sample was adjusted to two and the supernatant was separated from the settled heavy oil phase. The aqueous phase of the sample was extracted with dichloromethane then subjected to the same GC and IR analysis as for the previous extracted sample.

In the third sample of emulsion the acid fraction was isolated prior to analysis. The pH of a sample of emulsion was adjusted to two and extracted with dichloromethane. This organic phase was then back extracted with aqueous sodium hydroxide. The aqueous base extract containing salts of organic acids was then reacidified and extracted with dichloromethane to yield the acid fraction in an organic phase. This organic phase was evaporated down and dried with Na_2SO_4 before GC and IR analyses.

Figure 2-1 shows a summary of the three methods of sample preparation used.

2.2 Membrane Prescreening Tests

2.2.1 Membrane Description and Criteria for Selection

A total of twenty membranes of different porosities and of six different materials were examined during the prescreening tests. Table 2-1 shows the membrane type, manufacturer, trade name, and molecular weight cut off or estimated pore size for each of the membranes tested.

All twenty membranes were evaluated for pure water and salt water flux, and 15 of the membranes were evaluated during the emulsion prescreening test. The polyethelene glycol (PEG) test was conducted using six membranes after emulsion prescreening tests had identifed the best membranes of each type. Membrane G10, CA-20K, E500, RC-51, Cat, and PVDF were tested during the PEG test.

The purpose of the prescreening tests was to identify the specific membrane of each type most appropriate for use in this application and to characterize the membranes with respect to the standard parameters of productivity, salt rejection, and molecular weight cut off.

The selection of the specific membranes of each type was based primarily on the results obtained from the emulsion prescreening test. The desired membrane characterisitics from the emulsion prescreening test were:

i) rejection of oil,

ii) a stable flux rate,

FIGURE 2 - 1

PREPARATION OF EMULSION SAMPLES FOR GC & IR ANALYSIS

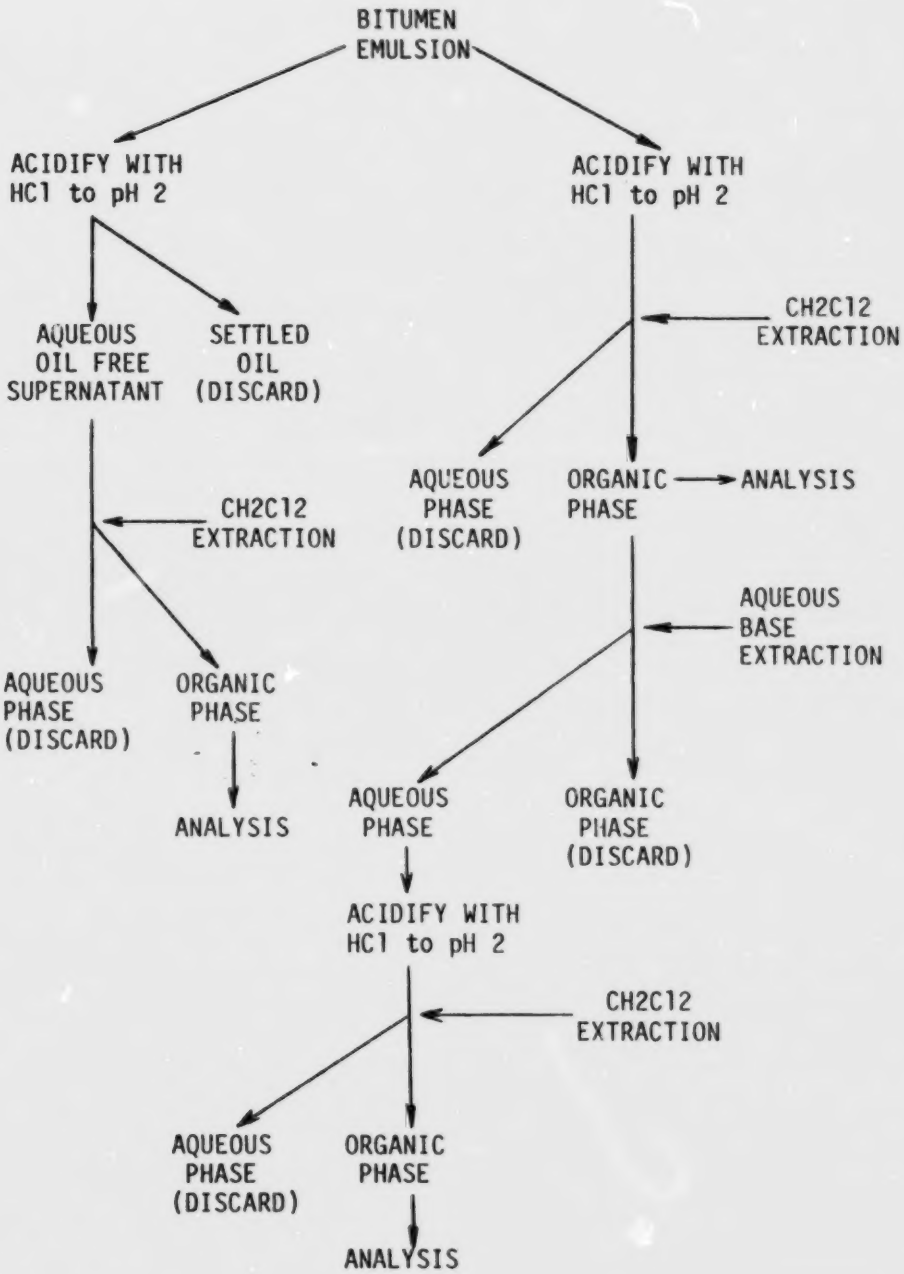


TABLE 2 - 1

MANUFACTURERS DESCRIPTION OF MEMBRANES USED

MEMBRANE TYPE	MANUFACTURER	TRADE NAME	MOLECULAR WT CUT OFF OR PORE SIZE
CELLULOSE ACETATE	OSMONICS	SEPA-0(CA)	1000 MW
	OSMONICS	SEPA-20(CA)	20000 MW
	OSMONICS	SEPA-50(CA)	50000 MW
	DESALINATION	CA - UF	20000 MW
POLYSULFONE	OSMONICS	SEPA-0K(PS)	1000 MW
	OSMONICS	SEPA-20K(PS)	20000 MW
	OSMONICS	SEPA-50K(PS)	50000 MW
	DESALINATION	E500	500 Angstroms
CHP (proprietary)	ZENON	Cat	20000 MW
		B2	10000 MW
		B3	10000 MW
CELLULOSE	S. AND S.	RC - 51	50 Angstroms
	*	12	NA
	*	13	NA
	*	23	NA
THIN FILM COMPOSITE	DESALINATION	G5	5 Angstroms
	DESALINATION	G10	10 Angstroms
	DESALINATION	G20	20 Angstroms
	DESALINATION	G50	50 Angstroms
POLYVINYLDIFLUORIDE	ABCOR	HF - 100 (P521)	10000 MW

S. AND S. (SCHLEICHER AND SCHUELL)
* SUPPLIED BY DR. T MATSUURA , NRC DIV. OF CHEM.

iii) a high flux rate, and

iv) rejection of organic carbon.

2.2.2 Pure Water Flux Test

2.2.2.1 Apparatus

The pure water flux tests were conducted using three National Research Council (NRC) test cells each with a membrane surface area of 13.3 cm^2. The flow in these cells enters from the outer edge of a circular membrane sheet and flows across the membrane surface to an exit port at the centre. The membrane is supported on a sintered stainless steel support plate. Figure 2-2 shows the design of the NRC tests cell units.

The test system had a 20 L process tank which fed an Osmonics, Tonka Flo centrifuged pump model #SB520X4200. The flow to each of the cells was maintained at 2 L/min. by allowing excess flow from the pump to return to the process tank via a by-pass line. The flow in the by-pass line was regulated manually with a needle valve. The pressure in the cells was maintained at the desired level using a back pressure regulating valve downstream from the cells. The temperature of the water in the system was controlled using cooling coils in the process tank. Heat was provided by the process pump. Figure 2-3 shows a flow schematic for the test apparatus.

2.2.2.2 Procedure

Samples of the membranes were placed in the NRC cells and the system was operated using pure water. The pure water was reverse osmosis (RO) permeate generated using tap water as a feed.

Figure 2 - 2

NRC TEST CELLS

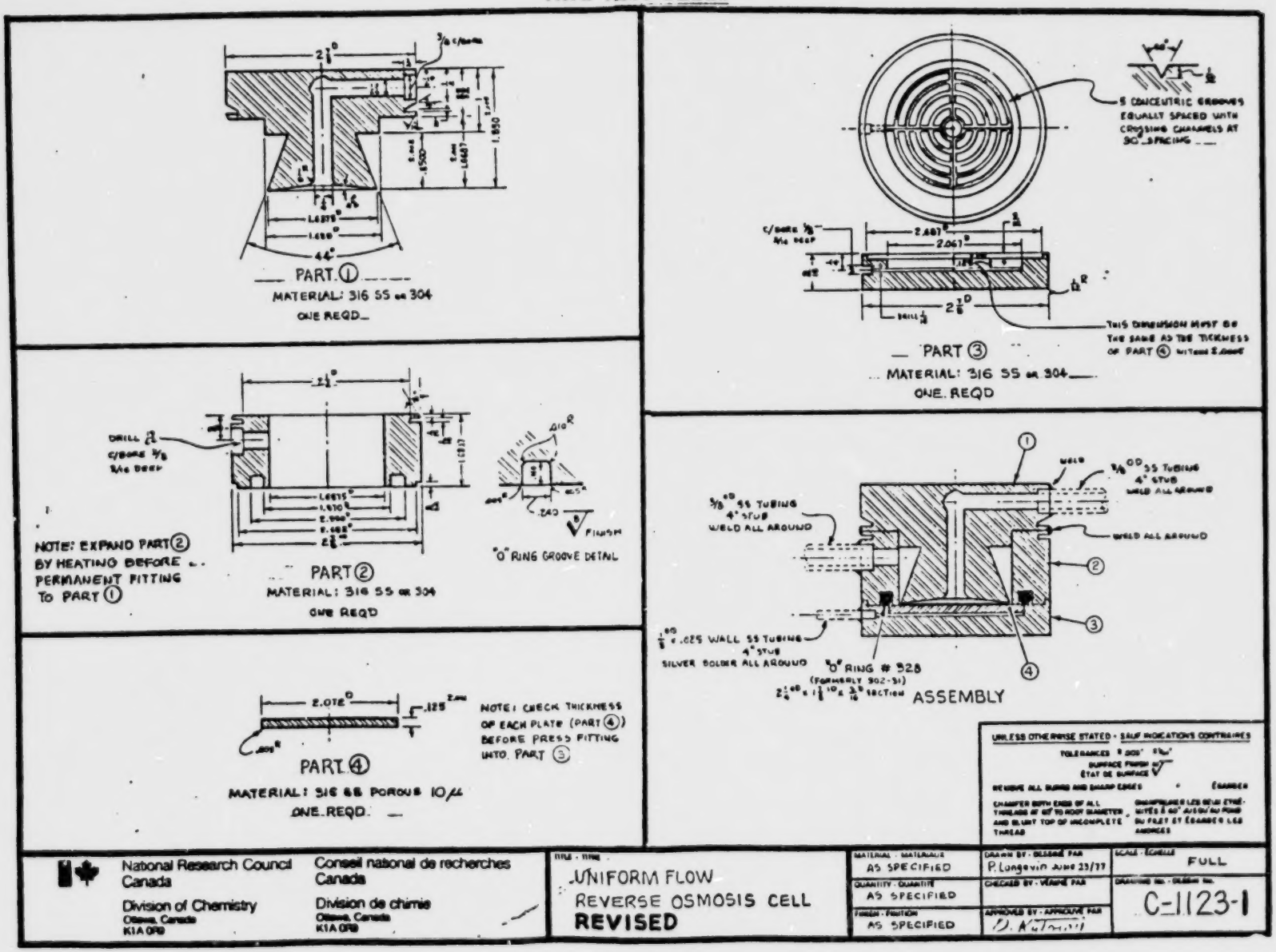
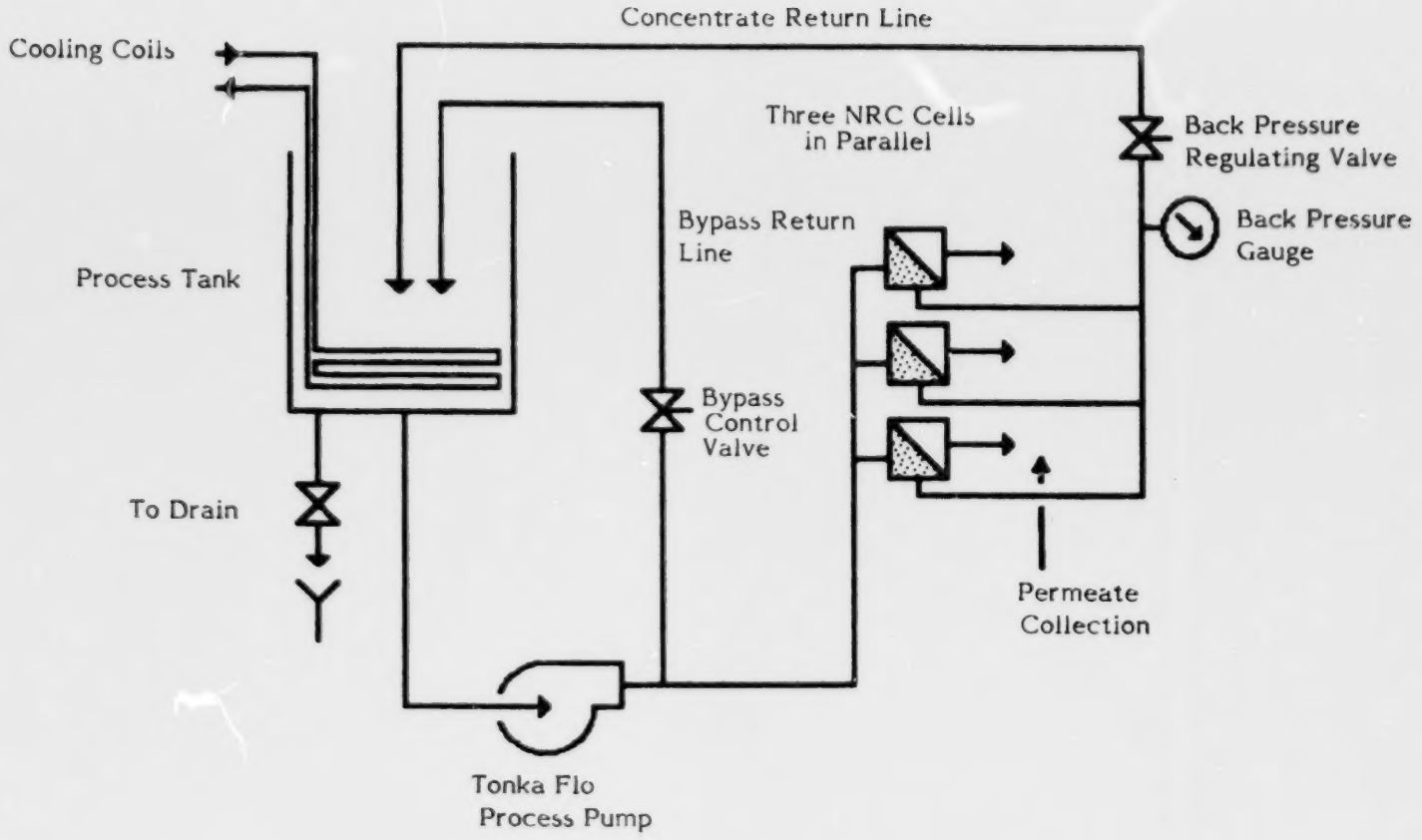

PART ①
MATERIAL: 316 SS or 304
ONE REQD
5 CONCENTRIC GROOVES EQUALLY SPACED WITH CROSSING CHANNELS AT 90° SPACING
PART ③
MATERIAL: 316 SS or 304
ONE REQD
THIS DIMENSION MUST BE THE SAME AS THE THICKNESS OF PART ④
NOTE: EXPAND PART ② BY HEATING BEFORE PERMANENT FITTING TO PART ①
PART ②
MATERIAL: 316 SS or 304
ONE REQD
"O" RING GROOVE DETAIL
WELD ALL AROUND
⅜" OD SS TUBING 4" STUB
⅛" OD x .025 WALL SS TUBING 4" STUB
SILVER SOLDER ALL AROUND
"O" RING # 328
(FORMERLY 302-31)
ASSEMBLY
PART ④
MATERIAL: 316 SS POROUS 10μ
ONE REQD
NOTE: CHECK THICKNESS OF EACH PLATE (PART ④) BEFORE PRESS FITTING INTO PART ③
UNLESS OTHERWISE STATED · SAUF INDICATIONS CONTRAIRES
REMOVE ALL BURRS AND SHARP EDGES · ÉBARBER
CHAMFER BOTH ENDS OF ALL THREADS AT 45° TO ROOT DIAMETER AND BLUNT TOP OF INCOMPLETE THREAD
National Research Council Canada
Conseil national de recherches Canada
Division of Chemistry
Ottawa, Canada K1A 0R9
Division de chimie
Ottawa, Canada K1A 0R9
UNIFORM FLOW
REVERSE OSMOSIS CELL
REVISED
MATERIAL · MATÉRIAUX: AS SPECIFIED
QUANTITY · QUANTITÉ: AS SPECIFIED
FINISH · FINITION: AS SPECIFIED
DRAWN BY · DESSINÉ PAR: P. Longevin June 23/77
CHECKED BY · VÉRIFIÉ PAR:
APPROVED BY · APPROUVÉ PAR: D. McTaggart
SCALE · ÉCHELLE: FULL
DRAWING NO. · DESSIN NO.: C-1123-1

Figure 2 - 3

FLOW SCHEMATIC FOR PURE WATER TEST APPARATUS



The system was operated with a pressure of 100 psi and at a temperature of 25°C for three hours. The system was allowed to operate for one hour before measurements of the flux rate were taken. This time allowed the flux rates to stabilize after initial compaction of the membrane. Flux rates were monitored and recorded periodically over the remainder of the test period.

2.2.3 Salt Water Flux Test

2.2.3.1 Apparatus

The apparatus used for the salt water flux test was the same as was used for the Pure Water Flux Tests described in section 2.2.2.1.

2.2.3.2 Procedure

Samples of the membranes were placed in the NRC test cells and the system was operated using a 1500 mg/L solution of NaCl as a feed to the cells. Ten liters of the salt solution was prepared using RO permeate with the appropriate amount of NaCl. The system was operated with a pressure of 100 psi and at a temperature of 25°C for three hours.

The conductivity of the feed and permeate and the flux rates were measured at regular intervals during the test. The procedure for conductivity measurement was the same as outlined for emulsion characterization in Appendix A.

The percent rejection of NaCl is calculated from:

$$R = \frac{C_f - C_p}{C_f} \times 100 \qquad (2\text{-}1)$$

where R = percent rejection

C_f = conductivity of the feed

C_p = conductivity of the permeate

The concentration of salt was maintained constant throughout the test by recycling both the permeate and the concentrate back to the process tank.

2.2.4 Emulsion Prescreening Tests

2.2.4.1 Apparatus

The emulsion prescreening tests were conducted using six NRC test cells arranged in parallel.

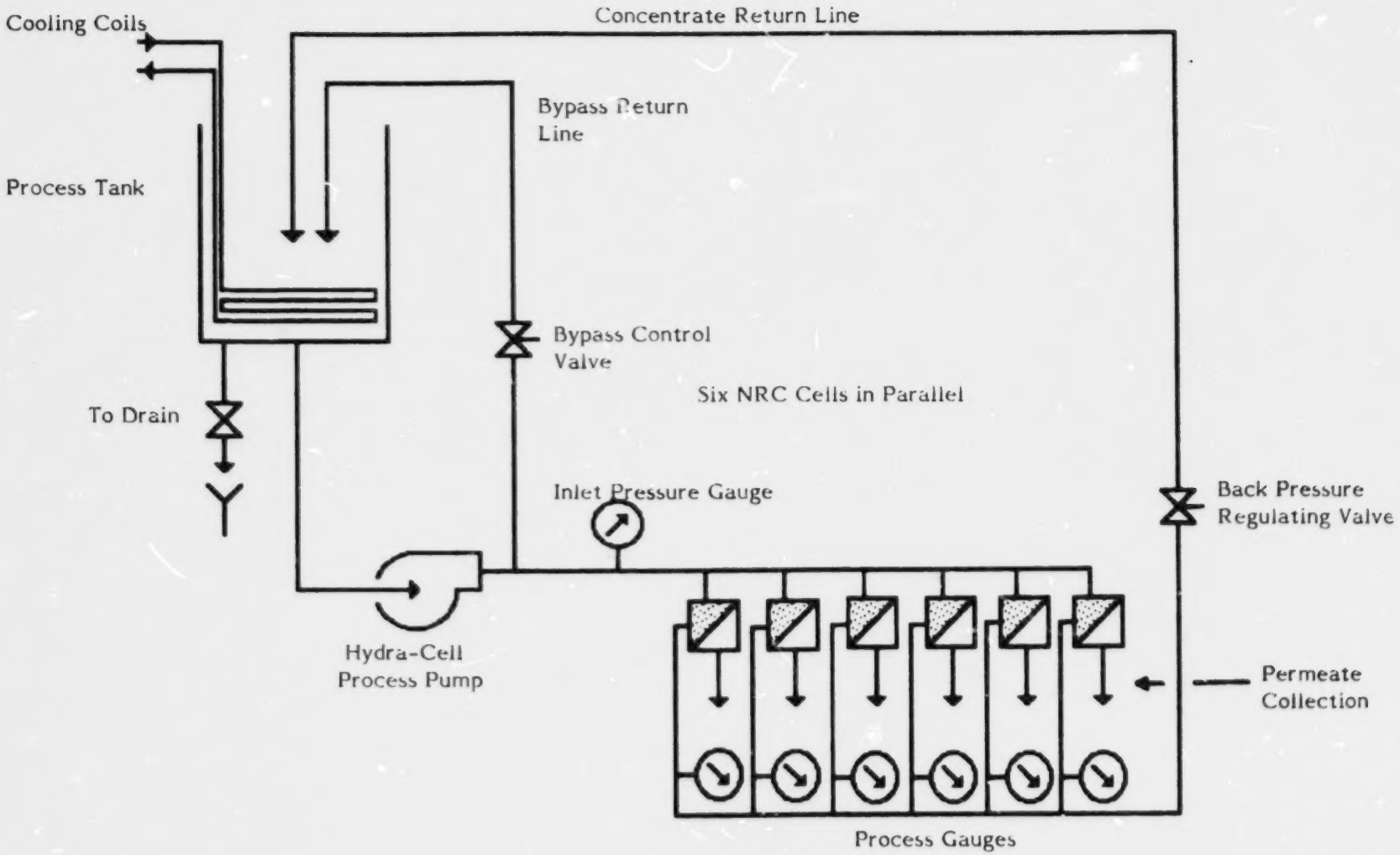
The 20 L process tank fed a hydra-cell pump model D-105516. The pump capacity was rated at 10 USGPM at 100 psi outlet pressure. As before, the flow to each of the cells was maintained at 2 L/min by manually adjusting a needle valve on a by-pass line from the pump outlet to the process tank. The temperature was controlled by manually adjusting the flow of water in cooling coils in the process tank. The pressure was controlled manually with a back pressure regulating valve on the concentrate return line. The pressure was measured on both the inlet and outlet to the NRC modules. A flow schematic for this system is shown in Figure 2-4.

2.2.4.2 Procedure

Samples of the membranes were placed in the NRC test cells and the system was operated using bitumen emulsion as a feed.

Figure 2 - 4

FLOW SCHEMATIC FOR EMULSION STABILITY TEST APPARATUS



The temperature of the feed was maintained at 25°C and the pressure to the cells was 100 psi. The tests were conducted for a period of 3 1/2 hours. Flux rates and samples of cell permeates were taken every 1/2 hour. The samples were analyzed for TOC using the procedure outlined in Appendix A. At the completion of the test samples of the feed and composite samples of permeate from each cell were analyzed for pH, conductivity, and TDS as per the procedures described in Appendix A.

2.2.5 Polyethelene Glycol (PEG) Test

2.2.5.1 Apparatus

The polyethelene glycol (PEG) tests were conducted using 6 NRC test cells set up in series.

The test system had a 20 L process tank which fed a Moyno Pump model ZM4 type SSF with a viton stator. As with previous systems the flow to the cells was maintained at 2 L/min by manually adjusting a needle valve on a by-pass line from the pump outlet to the process tank. The temperature was controlled by manually adjusting the flow of water in cooling coils in the process tank. The pressure to the cells was controlled with a back pressure regulating valve downstream of the final cell in series. The pressure at the outlet from the final cell was maintained at 100 psi and the pressure at the inlet of the first cell generally remained near 150 psi. A flow schematic for the system is presented in Figure 2-5.

2.2.5.2 Procedure

Samples of the membranes were placed in the NRC test cells and the system was operated using a 500 mg/L solution of a 6000 MW polyethelene glycol. The temperature of the system was maintained at 25°C and the pressure at the outlet was 100 psi. Tests were conducted for a period of one hour, during which time flux rates and samples of the permeate were taken at regular intervals. The samples were analyzed for TOC as before.

The percent rejection of PEG for each membrane was determined using.

$$R = \frac{C_f - C_p}{C_f} \times 100 \qquad (2\text{-}2)$$

where R = Percent Rejection

C_f = TOC feed concentration

C_p = TOC permeate concentration

The molecular weight cut off values for the membranes were determined by a comparison of percent rejections obtained with this test and those obtained with membranes of known molecular weight cut offs during previous membrane testing by ZENON staff.

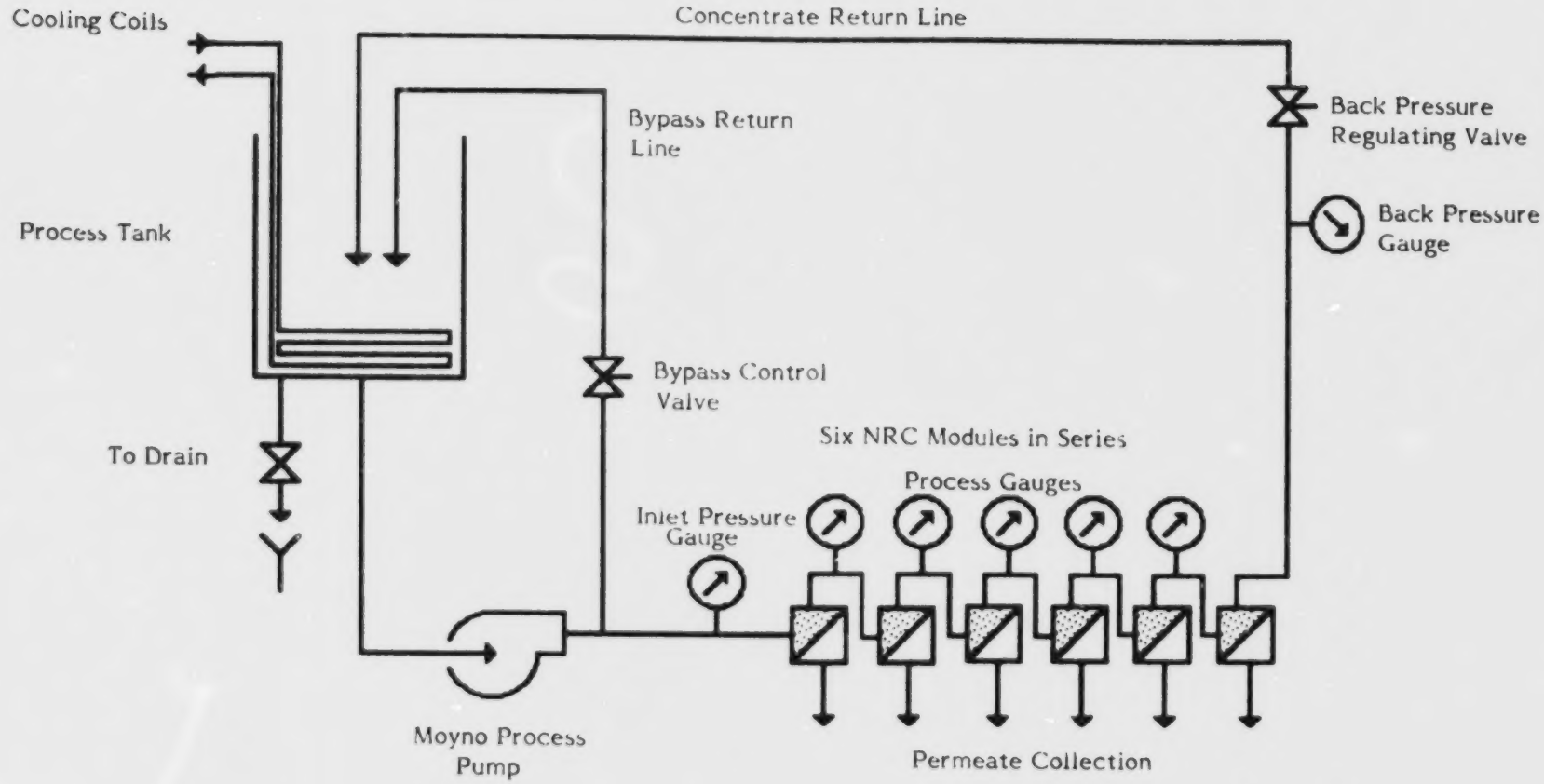
2.3 Membrane Screening Tests

2.3.1 Apparatus

The test apparatus used for the membrane screening tests was the same as that used for the PEG tests described in Section 2.2.5.1. A flow schematic for the system is shown in Figure 2-5.

Figure 2 - 5

FLOW SCHEMATIC FOR POLYETHELENE GLYCOL TEST APPARATUS



The Moyno pump was substituted for the Hydra-Cell for these tests because the values on the Hydra-Cell pump plugged with bitumen when operated for more than three or four hours. The particular Moyno used was limited to operation below 70°C because differential expansion of the components placed excessive strain on the pump motor. Moyno pumps capable of operating at higher temperatures are available.

2.3.2 Procedure

A total of 48 screening tests were conducted using the six different membranes chosen in the prescreening tests. In order to examine the effect of temperature and pH on membrane flux rates and permeate quality the feed to the system was maintained at different temperatures and adjusted to different pH values.

The temperature of the emulsion feed was controlled at 25°C, 45°C, or 65°C by adjusting the flow of cooling water to the coils in the process tank. Sixty five °C is considered to be the upper limit of most membrane system operation. The pH of the emulsion was either adjusted downwards to 5.5 with H_2SO_4, left as is at about 7.5, or adjusted upwards to 9.5 with NaOH. Table 2-2 shows a summary of all the screening tests performed and the operating conditions for each test.

Each of the screening tests was run for a period of 24 hours. During that time the flux rates were monitored every hour except for a period of about eight hours during the night. Composite samples of the permeate from each membrane and samples of the initial and final feed were collected and analyzed for the following parameters:

TABLE 2 - 2

OPERATING CONDITIONS FOR MEMBRANE SCREENING TESTS

RUN NO	TEMPERATURE (C)	pH	MEMBRANES
1	25	AS RECEIVED	TFC,CHP,PS,CA,PVDF,C
2	45	AS RECEIVED	TFC,CHP,PS,CA,PVDF,C
3	25	5.5	TFC,CHP,PS,CA,PVDF,C
4	45	5.5	TFC,CHP,PS,CA,PVDF,C
5	25	9.5	TFC,CHP,PS,CA,PVDF,C
6	45	9.5	TFC,CHP,PS,CA,PVDF,C
7	65	AS RECEIVED	TFC,CHP,PS,CA,PVDF,CHP
8	65	AS RECEIVED	PS ALL CELLS

TFC	THIN FILM COMPOSITE
CHP	ZENON MEMBRANE
PS	POLYSULPHONE
CA	CELLULOSE ACETATE
PVDF	POLYVINYL DIFLUORIDE
C	CELLULOSE

and final feed were collected and analyzed for the following parameters:

pH,

Conductivity,

Turbidity,

TOC,

TDS,

Ca and Mg,

Hardness, and

Dissolved Silica.

In addition to the regular analysis, the feed samples were analyzed for total suspended solids and a composite sample of the permeate from run number eight with PS membranes in all cells was subjected to detailed analysis for organics by GC & IR. The procedures for these analyses are presented in Appendix A.

Since each of the six cells in series had a slightly different applied pressure at the membrane surface the flux rates were adjusted to be equivalent to the flux rates at the inlet pressure using the formula

$$Q_i = Q_o \left(1 + \frac{P_i - P_o}{P_i}\right) \qquad (2\text{-}3)$$

where Q_i = Corrected Flux Rates or Flux Rate at Inlet Pressure

Q_o = Observed Flux Rate

P_i = Inlet Pressure

P_o = Observed Pressure in Cell

2.4 Batch Concentration Test

2.4.1 Apparatus

The apparatus for the batch concentration test was similar to that used for the PEG and membrane screening tests except that the by-pass line was set up to allow the by-pass flow to return to the process tank as before or to flow through a large plate and frame flat cell membrane test unit. This large cell unit contained four membranes each with a membrane surface area of 177 cm^2. Within the unit the four membranes were set up in parallel flow. The flow across each membrane entered one side of the rectangular membrane surface and flowed across the membrane and out near the side of the rectangle opposite to the feed side. This test unit was designed and manufactured by ZENON Environmental. Figure 2-6 shows the construction of the large cell test unit. Valves were put in place so that the by-pass flow could be directed to return directly to the process tank or to the process tank after passing through the large cell test unit. This large flat cell unit was used in order to achieve a higher concentration of the original feed more quickly than would have been possible using the NRC cells alone. A flow schematic for this equipment is shown in Figure 2-7.

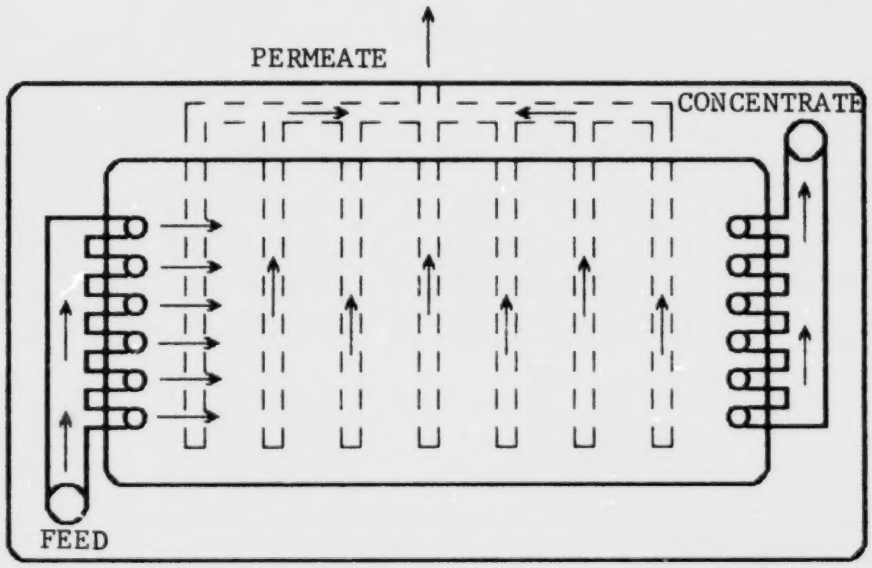
2.4.2 Procedure

Membranes G10, E500, and Cat were each placed in two NRC test cells in the test apparatus. Sheets of PVDF were also placed in the large cell test unit.

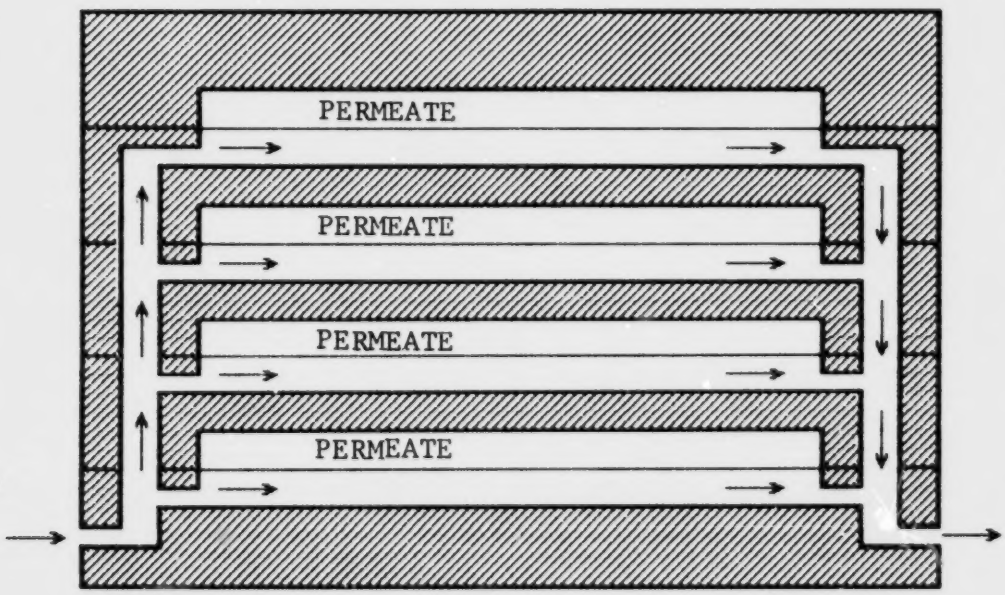
The pH of the bitumen emulsion feed was not adjusted and the temperature was maintained at 65°C. A flow to the NRC test cells of 2

FIGURE 2 - 6

PLATE AND FRAME MEMBRANE TEST UNIT



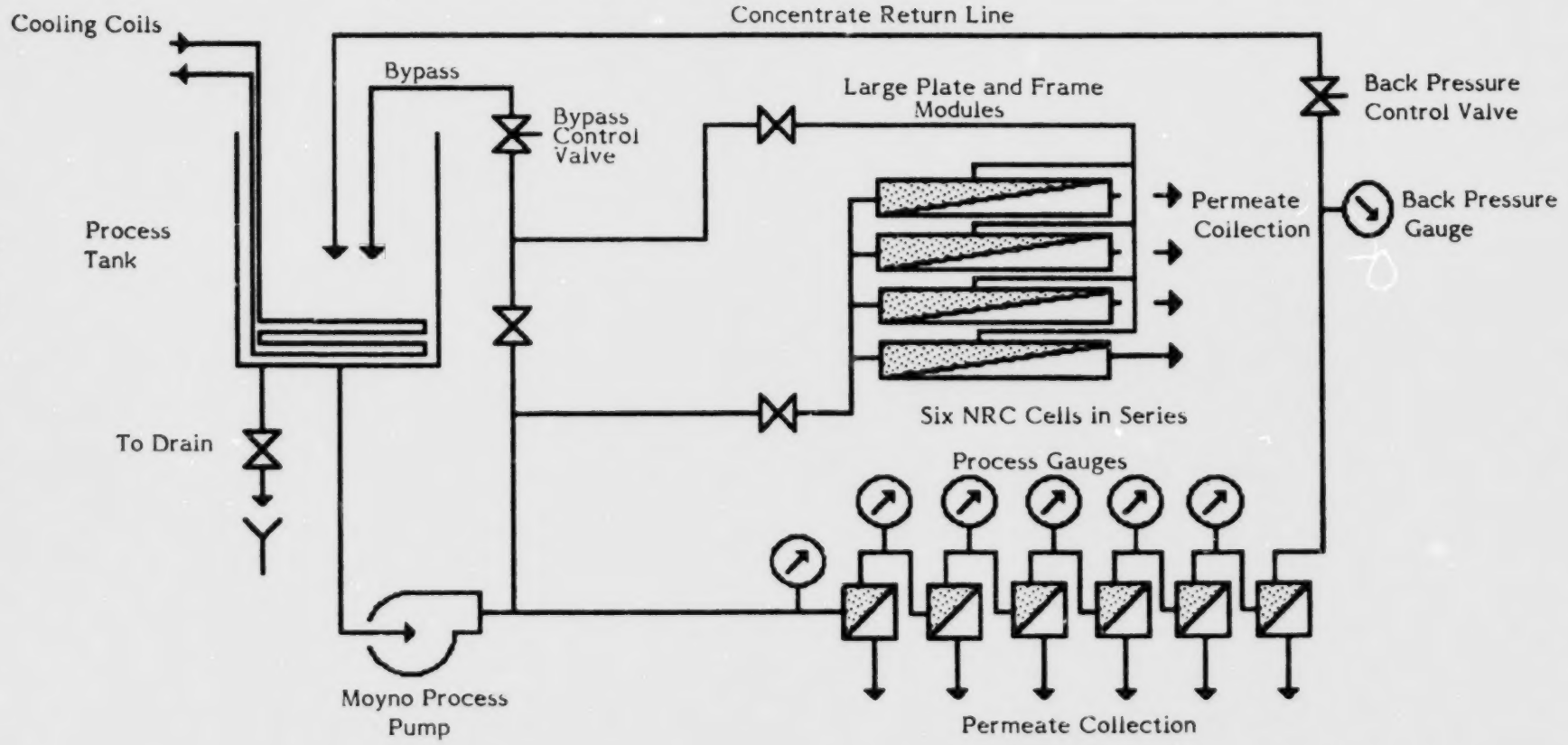
TOP VIEW OF INTERMEDIATE PLATE



SIDE VIEW OF TEST UNIT

FIGURE 2 - 7

FLOW SCHEMATIC FOR BATCH CONCENTRATION TESTS



L/min was maintained and the pressure at the outlet of the test cell was 100 psi.

The system was operated for a period of 50 hours with the permeate withdrawn from the system and the concentrate recycled to the process tank until the desired 90% volume reduction was obtained. During that time flux rates were monitored and samples of the permeate from the NRC test cells were taken at the start of the run, at 30%, 60%, and 90% volume reduction levels. These samples were analyzed for turbidity and TOC using the procedure outlined in Appendix A. Samples of the concentrated emulsion were removed from the process tank and allowed to stand for a period of several hours to determine if emulsion breaking was occurring.

The flux rates obtained for the NRC cells were adjusted for pressure by the same procedure used for the screening tests outlined in equation 2-3.

2.5 Long Term Stability Test

2.5.1 Apparatus

The apparatus for the long term stability test was the same as was used for the batch concentration test. During the long term stability test the valves on the by-pass line were set so that all the flow in the by-pass line returned directly to the process tank and did not pass through the large flat test cells.

2.5.2 Procedure

Once a 90% volume reduction was achieved in the batch concentration test the long term stability test began. The membranes

and operating conditions remained the same as during the concentration test. The flow in the system was changed so that the by-pass flow returned directly to the process tank. Both the permeate and the concentrate were also recycled to the process tank.

The system was operated for 300 hours after the 90% volume reduction was achieved. During this time the flux rates were monitored and samples of permeate from each of the membranes and from the feed tank were taken after one week and at the end of two weeks of operation. These samples were analyzed using procedures outlined in Appendix A for the following:

pH,

Conductivity,

Turbidity,

TOC,

TDS,

Dissolved Silica,

Ca and Mg, and

Hardness,

The samples of feed were also analyzed for total suspended solids (TSS) and total suspended oil (TSO). The flux rates obtained were adjusted for pressure using equation 2-3.

2.6 Reverse Osmosis Tests

2.6.1 Apparatus for RO Tests

The reverse osmosis tests were all conducted using the large plate and frame flat cell membrane test unit which was used for the

batch concentration test described in Section 2.4.1. Figure 2-6 shows the construction of this membrane test unit.

The test system had a 20 L process tank equipped with cooling coils for maintaining the temperature of the feed at the desired level. The flow to the cooling coils was controlled automatically by a solenoid valve connected to a thermocouple in the process tank. The process tank fed a Hydra Cell Pump and the flow to the test unit was maintained at approximately 15 L/min by manually adjusting a needle valve on the by-pass line from the pump outlet to the process tank. The pressure was controlled manually with a back pressure regulating valve on the concentrate outlet of the test unit. The pressure at the outlet of the test unit was monitored.

A flow schematic for this system is shown in Figure 2-8.

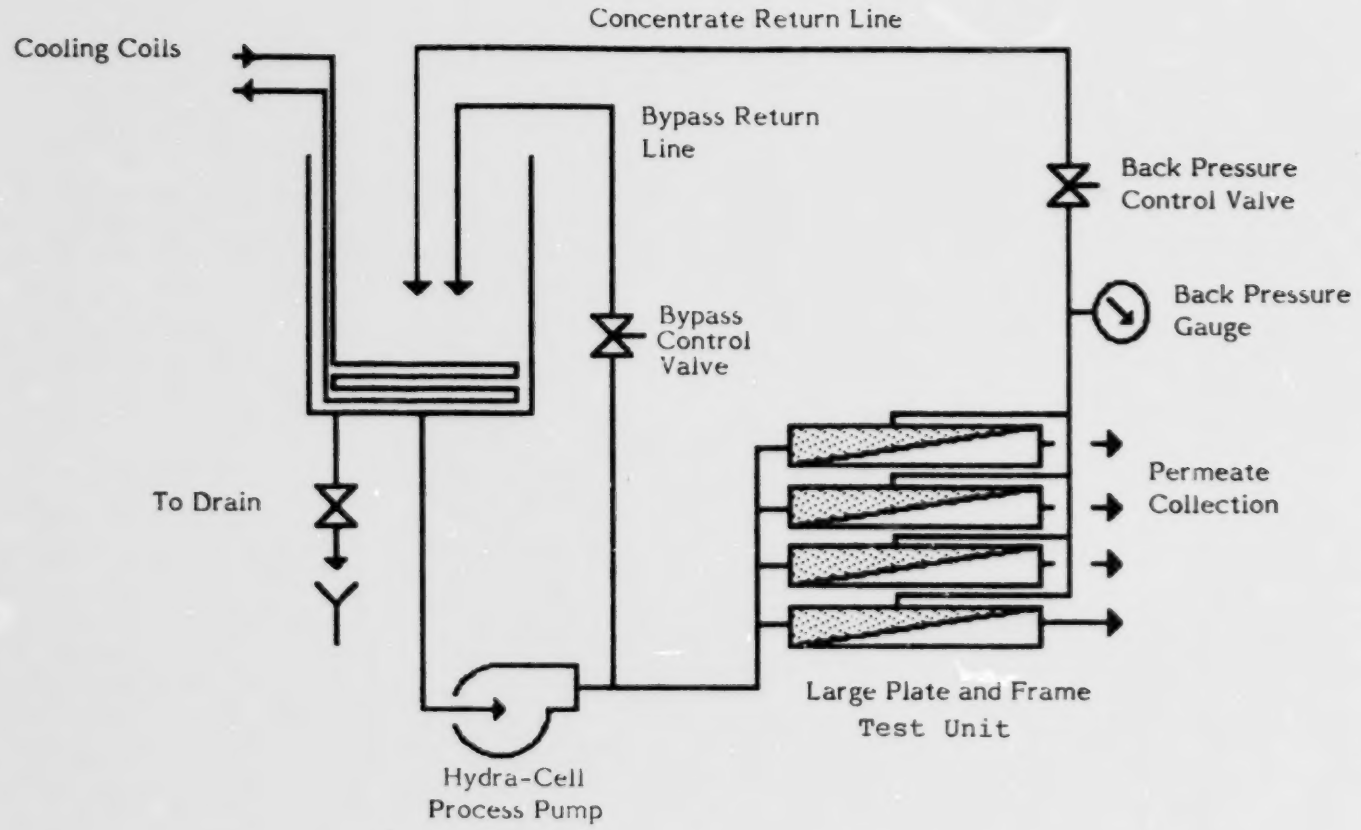
2.6.2 Reverse Osmosis Screening Test

Two different reverse osmosis membranes, a Filmtec FT30, thin film composite membrane and a cellulose acetate membrane (desalination), were used during the RO screening test. Sheets of each membrane were placed in two of the cells in the test unit.

A salt water flux test was performed on the cells in the test unit before testing with the UF permeate. A 1500 mg/L solution NaCl in RO water was feed to the system for a 4 1/2 hour period. The temperature of the feed was maintained at 25°C and the pressure to the cells was 400 psi. The flux rates and conductivity of the permeates from each cell and of the feed water were measured every half hour. The salt rejections were calculated using equation 2-1.

FIGURE 2 - 8

FLOW SCHEMATIC FOR R.O. TESTS



For the RO screening test the feed to the system was a composite sample of permeate generated during the final UF membrane screening test using a polysulfone membrane in each of the cells. The test was run for 4 1/2 hours with the temperature and pressure maintained at 25°C and 400 psi respectively. The conductivity and pH of the permeate from each cell and of the feed were measured every half hour. Flux rates were also measured every half hour.

A salt water flux test was performed on the membranes after completion of the test with UF permeate. The procedure used was the same as was used for the initial salt water test.

2.6.3 Reverse Osmosis Test on UF Permeate

Ultrafiltration permeate was generated by operating the large flat cell test unit with four sheets of the G10-TFC membrane. The operating temperature was 65°C and the pH of the emulsion feed was not adjusted. The system was operated until sufficient permeate was available for the RO test.

For the RO test, sheets of the Filmtec FT30, thin film composite seawater membrane were placed in each of the four cells of the test unit. An initial salt water flux test was performed on the test unit using the same procedure as was used during the screening test.

During the RO test on UF permeate the temperature of the feed was maintained at 25°C and the pressure to the cells was 400 psi. The test was run for just over five hours until a 90% volume reduction had been obtained. During the run flux rates were taken every 15 minutes and the conductivity of the permeate from each cell and of the

feed were also measured every 15 minutes. The pH of the permeates and feed were measured every 1/2 hour.

Samples of the feed were taken before the tests began and at the completion of the run. Samples of the combined permeate from the four cells were taken after 30 min and when 30%, 60%, and 90% volume reductions had been achieved. All six of these samples were analyzed for the following:

pH,
Conductivity,
Turbidity,
TOC,
TDS,
Dissolved Silica,
Anions
Cations, and
Hardness

Samples of the final feed and the permeate at a 90% volume reduction were also analyzed for alkalinity.

A salt water flux test was also performed on the membrane system after completion of the test with UF permeate. The procedure used was the same as that used previously.

2.6.4 Reverse Osmosis Test on Demulsified Bitumen Emulsion

Demulsified bitumen emulsion was obtained by treating a 40 L volume of emulsion with 250 ppm of the chemical demulsifier RTC 323. The emulsion was mixed and the heavy oil was allowed to settle.

The supernatant was then drained off and passed through a five micron cartridge filter.

The remainder of the procedure for the reverse osmosis test on the demulsified bitumen emulsion was identical to that used for the RO test on UF permeate.

3.0 RESULTS AND DISCUSSION

3.1 Sample Characterization

3.1.1 Particle Size Analysis

The particle size analysis on the raw emulsion yielded a mean particle size of 7.8 microns based on particle volume and 2.8 microns based on population. The clay anaysis was conducted on material which could not be extracted with toluene. The mean particle size of this material was 9.8 microns based on particle volume and 2.5 microns based on population. The clay material made up only 7% of the total particle population of raw emulsion. Particle size data for other sources of produced water emulsion are not available for comparison but the very fine droplet size is indicative of very stable emulsions. Particles in the 7-10 micron range will be rejected easily by a membrane with pore sizes less than 0.5 microns (500 angstroms).

Table 3-1 shows a summary of the results of the particle size analysis on the bitumen emulsion. The complete results of the analysis are presented in Appendix B.

3.1.2 Emulsion Stability

Effect of pH

Samples of the standard bitumen emulsion showed no sign of emulsion destabilization at pH values of 4.5, 5.0, 5.5, 6, 8, 10, or 12. When the pH of a sample was adjusted to 4.0 the emulsion broke and a heavy oil layer settled within 2 hours. The supernatant was relatively free of suspended particles but retained a yellow tint. The settled oil compacted to about 10% of the total volume of sample. Another sample of emulsion in which pH was adjusted to 2 also broke

TABLE 3 - 1

RESULTS OF PARTICLE SIZE ANALYSIS
OF PRODUCED WATER EMULSION

FRACTION	PARTICLES PER (ml) OF SOLUTION	MEAN PARTICLE SIZE (MICRONS) BASED ON VOL %	MEAN PARTICLE SIZE (MICRONS) BASED ON POPULATION
RAW	4,744,000	7.8	2.8
CLAY (TOLUENE WASHED)	341,000	9.8	2.5
OIL (RAW-CLAY)	4,403,000	7.8	2.5

and a heavy oil layer settled within one hour. The supernatant from the pH 2 sample was clearer than that of the pH 4 sample and had a less intense yellow tint.

Samples of the three high oil content bitumen emulsions (refered to as P35, P33, and PI-11) each had their pH adjusted to 3.0, 3.5, and 4.0. Sample P35 showed no signs of separation at pH 4 or pH 3.5 and only slight separation at a pH of 3. Sample P33 showed no separation at pH 4, slight separation at pH 3.5, and clear separation at pH 3.0. Sample PI-11 showed no separation at pH 4 or pH 3.5 but clear separation at pH 3.0.

Table 3-2 shows a summary of the emulsion stability tests with respect to pH. It is beleived that the emulsions break at low pH as the polar surfactant which is substantially responsible for maintaining the stable emulsion becomes inactive at low pH. It is certainly technically feasible to break the emulsion entirely by lowering the pH substantially but this practice may be undesirable for downstream processes. Slight pH adjustment ($\pm$ 2 pH units) to help destabilize emulsions is often employed in industrial oily water separations using membranes. The combination of a destabilized and concentrated emulsion often allows for oil to be skimmed off in the process tank. Such an approach was not useful in this case because a more drastic pH reduction was needed to effect any change in emulsion stability.

TABLE 3 - 2

STABILITY OF BITUMEN EMULSIONS
WITH RESPECT TO pH

pH	STANDARD EMULSION	HIGH OIL P35	HIGH OIL P33	HIGH OIL PI-11
4.5 AND ABOVE	NO SEPARATION	NOT DONE	NOT DONE	NOT DONE
4.0	CLEAR SEPARATION	NO SEPARATION	NO SEPARATION	NO SEPARATION
3.5	NOT DONE	NO SEPARATION	SLIGHT SEPARATION	NO SEPARATION
3.0	NOT DONE	SLIGHT SEPARATION	CLEAR SEPARATION	CLEAR SEPARATION
2.0	CLEAR SEPARATION	NOT DONE	NOT DONE	NOT DONE

Effect of Freezing

The sample of emulsion which was frozen and allowed to thaw had a distinct heavy oil layer which settled out but the upper layer was still dark brown and somewhat cloudy.

Effect of Heating

The sample of emulsion which was heated to 100°C for a half hour showed little sign of emulsion destabilization. Increasing emulsion temperature will frequently destabilize less tightly bound emulsions.

Effect of Chemical Demulsifiers

Chemical demulsifiers are used commercially in many applications including produced water treatment. The concentration of demulsifiers required is critical to the economics of large systems. The chemical demulsifier RTC 323 was successful in breaking the emulsion at concentration levels of 1000 and 250 ppm. Clear separation of the heavy oil and the supernatant occured within 10 minutes of the addition of the demulsifier. At a concentration level of 62.5 ppm, the demulsifier had no effect on the emulsion even after several hours. Demulsifiers RTC 326, RTC 327, and RTC 330 each had no effect on the emulsion at concentration levels of 1000 ppm.

It had been suggested by the supplier that the emulsion breaking capabilities of Witco demulsifiers were enhanced by the presence of $ZnCl_2$ in solution.

Chemical demulsifiers complexed with $ZnCl_2$ acted differently from uncomplexed demulsifiers. The emulsion breaking

mechanism of RTC 323 was somehow blocked by the $ZnCl_2$ in solution. RTC 323 in solution with $ZnCl_2$ was ineffective in breaking the bitumen emulsion.

RTC 326 and RTC 330 required the $ZnCl_2$ to function as demulsifiers. RTC 326 at 1000 ppm with $ZnCl_2$ at 200 ppm broke the bitumen emulsion and clear separation of the heavy oil occured within about 15 minutes. RTC 326 at 250 ppm with $ZnCl_2$ at 50 ppm was also effective in breaking the emulsion. At levels of 62.5 and 12.5 ppm no emulsion breaking occured. RTC 330 acted in an identical manner to RTC 326 and worked well at 1000 ppm with 200 ppm of $ZnCl_2$ and at 250 ppm with 50 ppm of $ZnCl_2$ but did nothing at 62.5 ppm with 12.5 ppm $ZnCl_2$. RTC 327 had no effect on emulsion stability at 1000 ppm complexed with 200 ppm $ZnCl_2$. Table 3-3 shows a summary of the results of demulsifier tests on the bitumen emulsion.

Since RTC 323 alone performed as well as RTC 326 and RTC 330 complexed with $ZnCl_2$, RTC 323 was chosen as the demulsifier to be used to break the emulsion for the reverse osmosis test on the broken emulsion.

3.1.3 Standard Analytical Parameters

Results of the analyses of bitumen emulsions are presented in Table 3-4. The table includes results of analyses performed on the standard emulsion at the start of experimental work and at the start of the batch concentration tests and that performed on the three high oil content samples. Also presented in the table are typical values for such emulsions as given by CH2M HILL (1982).

TABLE 3 - 3

EFFECT OF CHEMICAL DEMULSIFIERS ON BITUMEN EMULSION

DEMULSIFIER	CONCENTRATION	RESULT
RTC 323	1000 ppm	Clear Separation, oil sinks
RTC 323	250 ppm	Clear Separation, oil sinks
RTC 323	62.5 ppm	No separation
RTC 326	1000 ppm	No separation
RTC 327	1000 ppm	No separation
RTC 330	1000 ppm	No separation
RTC 323 +ZnCl 2	1000 ppm 200 ppm	No separation
RTC 326 +ZnCl 2	1000 ppm 200 ppm	Clear Separation, oil sinks
RTC 326 +ZnCl 2	250 ppm 50 ppm	Clear Separation, oil sinks
RTC 326 +ZnCl 2	62.5 ppm 12 ppm	No separation
RTC 327 +ZnCl 2	1000 ppm 200 ppm	No separation
RTC 330 +ZnCl 2	1000 ppm 200 ppm	Clear Separation, oil sinks
RTC 330 +ZnCl 2	250 ppm 50 ppm	Clear Separation, oil sinks
RTC 330 +ZnCl 2	62.5 ppm 12 ppm	No separation

Witco Chemical refers to agents which are designed for separating oil in water emulsions as reverse demulsifiers. The demulsifiers used in these experiments are described as reverse demulsifiers by Witco Chemical.

TABLE 3 - 4

EMULSION CHARACTERIZATION RESULTS

PARAMETER	HIGH OIL CONTENT EMULSIONS P33	P35	P1-11	INITIAL CHARAC.	FINAL CHARAC.	TYPICAL EMULSION
pH	8.16	8.25	8.28	8.01	7.75	6.8 - 8.6
TOC mg/L	16568	24265	703	1560	880	NA
FOC mg/L	359	1169	565	260	165	NA
TDS mg/L	333 *	833 *	1595 *	716	784	844 - 31349
TDO mg/L	NA	NA	NA	124	282	NA
TSO mg/L	26900	22300	5500	1580	1602	96 - 2000
TSS mg/L	450	17216	214	40	34	68 - 447
Naphthenic Acid mg/L	NA	NA	NA	60	NA	NA
SILICA total mg/L	<100	<120	<100	100	56.14	8 - 380
diss. mg/L	91	77	84	100	82.16	NA
Calculated Hardness as CaCO3 mg/L	12.36	11.37	53.27	3.93	3.78	41 - 890
Turbidity (NTU)	34000	44000	190	1150	975	NA
Anions						
Fluoride mg/L	5.2	6.2	4.2	4.13	3.4	NA
Chloride mg/L	360	240	410	142	148	199 - 13348
Nitrite mg/L	<1	<1	<1	NA	<4	NA
Phosphate mg/L	<.01	<.01	<.01	<10	<1	NA
Nitrate mg/L	<.4	<.4	<.04	<.5	<1	0 - 0.3
Sulphate mg/L	119	77	147	66.7	58	22 - 525
Cations						
Beryllium mg/L	0.015	0.006	<.005	<.0005	<.01	NA
Molybdenum mg/L	1.1	1.33	0 178	<.2	0.08	NA
Calcium mg/L	3.4	3.3	17	1.16	1.1	48 - 290
Vanadium mg/L	20.9	19.5	1.15	0.012	0.32	NA
Aluminum mg/L	1.58	1.00	1.06	1.22	0.96	NA
Magnesium mg/L	0.94	0.76	2.64	0.25	0.25	5 - 156
Barium mg/L	0.07	0.063	0.23	0.011	0.13	NA
Potasium mg/L	7.6	6.3	19.9	6	6.5	NA
Strontium mg/L	0.115	0.093	0.78	0.010	<.01	NA
Sodium mg/L	300	265	385	245	225	215 - 11007
Zinc mg/L	0.13	0.12	0.28	<.05	0.05	NA
Cadmium mg/L	0.02	0.02	0.04	<.01	<.01	NA
Manganese mg/L	0.12	0.03	0.83	0.02	0.05	NA
Cobalt mg/L	0.06	0.02	0.02	<.05	<.05	NA
Copper mg/L	0.04	0.01	0.31	0.073	0.05	NA
Silver mg/L	0.02	<.03	<.03	<.005	<.02	NA
Iron mg/L	1.44	0.93	2.4	7.92	71	0.1 - 1.0
Lead mg/L	0.12	0.04	0.18	<.05	<.02	NA
Chromium mg/L	0.3	0.23	0.14	<.01	0.06	NA
Nickel mg/L	6.5	6.3	0.62	<.05	0.13	NA

TOC total organic carbon
FOC filtered organic carbo
TDS total dissolved solids
* the values include TDS+TDO
TSO total suspended oil
TSS total suspended solids
TDO total dissolved oil
Hardness is calculated from Ca & Mg
NA - DATA NOT AVAILABLE
TYPICAL EMULSION CHARACTERIZATION DATA IS FROM CH2M HILL (1982)

The results for the standard emulsion show an extremely low hardness of 4 mg/L. Typical hardness values for emulsions are reported in the range between 41 and 890 mg/L (CH_2M HILL, 1982). The hardness of the three high oil content samples were 11, 12, and 53 mg/L. Some variability at the Texaco site is apparent but all of the values are below or in the lower end of the range of typical values.

Other components in the standard emulsion sample fall within or near the typical range. The three high oil samples show considerable variability in TOC, TDS, TSO, TSS, and turbidity.

The iron contents of the three higher oil samples were 0.93, 1.44, and 2.4 mg/L. The iron contents determined in the initial and final analyses of the standard emulsion were 8 mg/L and 71 mg/L respectively. The nine fold increase in iron between the time of the initial and final analyses is believed to be the result of iron leaching out from the metal storage drums. It is likely that the 8 mg/L determined initially is also somewhat elevated as a result of leaching from the metal drum. The high oil content samples were shipped in plastic containers and analyzed soon after they arrived. The iron content determined should accurately represent the iron present in the emulsion when it was sampled. The stability of the standard emulsion appeared unaffected over time with the increasing concentration of iron.

Oil and grease and ethyl acetate extractable surfactant yielded a total of 1705 mg/L of oil and grease and 218 mg/L of surfactant. The oil and grease value, which was determined by freon extraction is very close to the 1620 mg/L obtained by the method used for TSO and TDO in previous analyses.

3.1.4 GC and IR Analysis

Gas chromatographic (GC-FID) analysis of the pH 2 emulsion sample extracted with CH_2Cl_2 showed no distinctive peaks and therefore conclusions about the content of the sample are difficult to make.

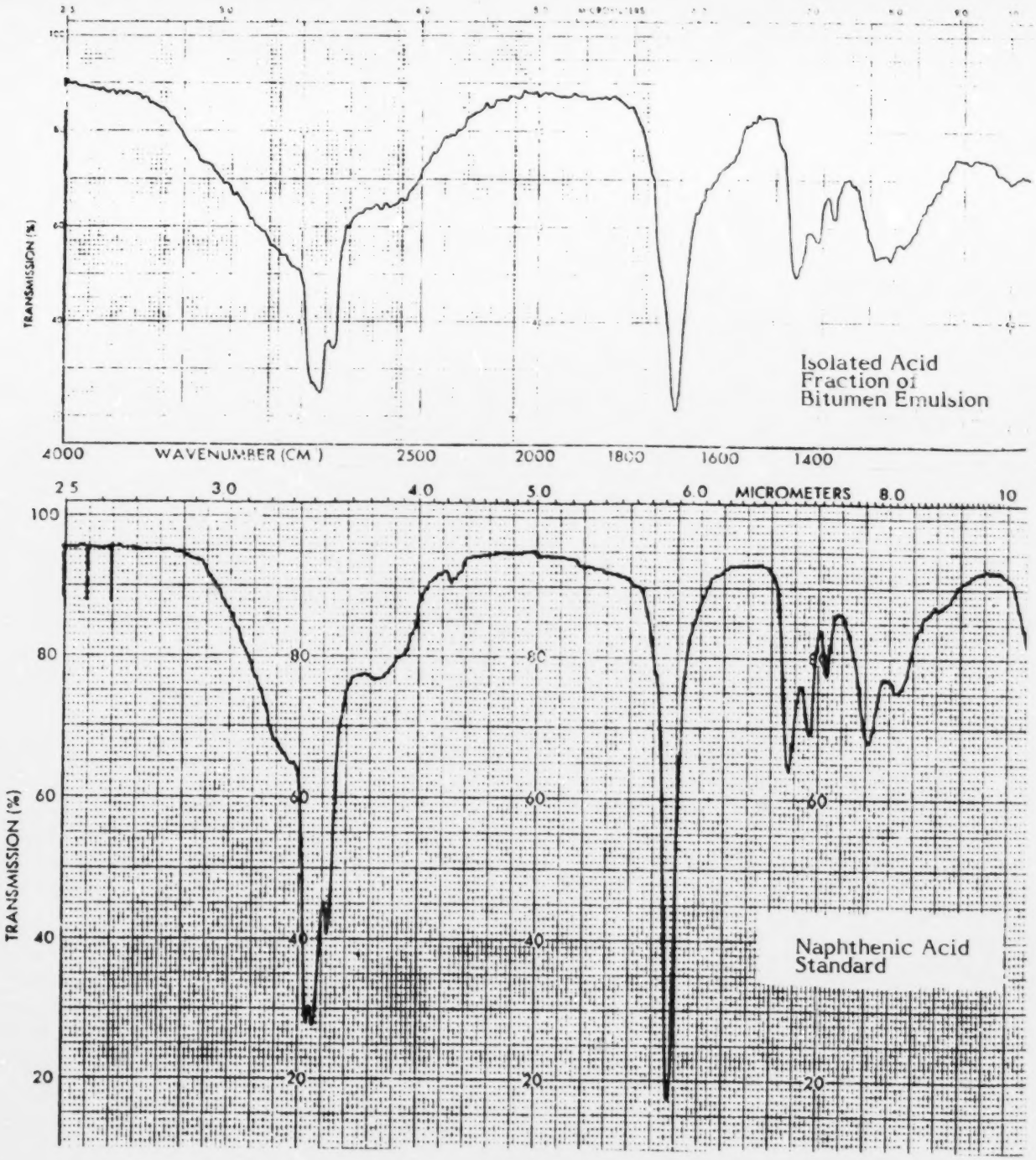
Infra-red spectrophotometric analysis (IR) of the residue on the IR plate after evaporation of solvent gave a spectrum with very broad adsorptions. A definite O-H stretch at 3800 - 2800 cm^{-1} is present. Absorptions at 2000 cm^{-1} and 1760 - 1500 cm^{-1} are also present but unambiguous assignment is not possible. A wide band between 1760 - 1500 cm^{-1} is felt to be carbonyl. A saturated aliphatic C-H stretch is observed at 2970 cm^{-1}. No other adsorption bands are visible. The IR spectra for these tests are presented in Appendix B.

GC analysis of the aqueous supernatant of the broken bitumen emulsion at pH 2 showed a large hump commonly associated with naphthenic acids. The size of this hump indicated a concentration of 13 mg/L of naphthenic acid in the sample. IR analysis showed a strong OH stretch associated with organic acids at 1700 - 1740 cm^{-1} and peaks at 1450, 1410, and 1370 cm^{-1}. All these peaks are consistent with the presence of naphthenic acid in the sample.

The third emulsion sample was back extracted to eliminate interference from other non acidic organic components. IR analysis of the back-extracted sample of bitumen emulsion showed an exact match to a naphthenic acid standard. Figure 3-1 shows the IR scan for the isolated acid fraction of the emulsion and for a naphthenic acid standard. GC analysis showed the presence of 60 mg/L of naphthenic acid.

FIGURE 3 - 1

INFRARED SCAN OF ISOLATED ACID FRACTION OF
BITUMEN EMULSION AND NAPHTHENIC ACID STANDARD



It is beleived that the naphthenic acids present in the emulsion are primarily responsible for maintaining the very high stability of the emulsion. When the pH of the emulsion is lowered, aqueous phase solubility is lowered and much of the naphthenic acid passes into the oil phase and is no longer active as a surfactant. This is illustrated by the fact that the aqueous supernatant of the pH 2 emulsion contained only 13 mg/L of naphthenic acid, considerably less than the 60 mg/L present in the isolated acid fraction of the bitumen emulsion.

3.2 Membrane Prescreening Test

3.2.1 Pure Water Flux Tests

A summary of the results of the pure water flux tests on the 20 membranes is shown in Table 3-5. Complete results presented in Appendix C. The results give an indication of the flux rates obtainable with each membrane. The polysulfone (PS) and CHP membranes consistently gave the highest flux rates. Flux rates for TFC membranes increased as the pore sizes of the membranes increased. The cellulose acetate (CA) membrane 50K has a much lower flux than the CA - 0K or 20K membrane. The lower flux of the larger pore membrane is believed to be the result of a different backing material used with CA - 50K restricting the flux rate.

3.2.2 Salt Water Flux Test

A summary of the results of the salt water flux test is presented in Table 3-6. Complete results are presented in Appendix C. These results give a furtner indication of potential flux rates

TABLE 3 - 5

RESULTS OF PURE WATER FLUX TESTS

MEMBRANE	AVERAGE FLUX RATE M3/M2 D	MEMBRANE	AVERAGE FLUX RATE M3/M2 D
TFC G5	0.31	PS-OK	12.29
G10	1.24	20K	16.62
G20	3.10	50K	15.13
G50	11.26	E500	16.46
CA-OK	3.36	CELLULOSE 12	0.47
20K	6.04	13	3.23
50K	1.72	23	1.72
UF	1.14	RC-51	0.20
C.H.P. Cat	19.50	PVDF	5.91
B2	11.31		
B3	13.12		

Operating Temperature = 25 deg. C
Operating Pressure = 100 psi (712 KPa))

TABLE 3 - 6

RESULTS OF SALT WATER FLUX TESTS

MEMBRANE	AVERAGE FLUX RATE M3/M2 D	% REJ	MEMBRANE	AVERAGE FLUX RATE M3/M2 D	% REJ
TFC G5	0.28	71.43	PS-OK	14.28	7.14
G10	0.96	72.81	20K	14.44	9.70
G20	2.67	50.38	50K	49.32	11.82
G50	1.03	72.67	E500	13.96	13.96
CA-OK	6.41	1.70	CELLULOSE 12	0.40	6.70
20K	5.66	0.00	13	0.19	18.81
50K	1.60	48.57	23	1.22	5.02
UF	11.28	9.72	RC-51	0.17	20.58
C.H.P. Cat	15.43	74.35	PVDF	4.61	10.02
B2	11.56	88.91			
B3	12.40	26.59			

Operating Temperature = 25 deg. C
Operating Pressure = 100 psi (712 KPa)

through each membrane and an indication of the percent rejection of monovalent ions each membrane can achieve. As in the pure water flux tests the flux rates for PS and CHP membranes were consistently higher than for all other membranes. The salt rejections for the PS membranes were however consistently much poorer than for the CHP membranes. Three membranes were dropped at this point because of consistently poor performance during these tests. The membranes not included in further work were TFC-G5, CA-UF, and PS-OK.

3.2.3 Emulsion Prescreening Test

Figures 3-2, 3-3, and 3-4 show the flux rate results of the emulsion prescreening tests. Table 3-7 shows the efficiency of each membrane in rejecting the TOC present in the bitumen emulsion during the prescreening test. Complete results of these tests are presented in Appendix C.

The pure water and salt water tests yield information on membrane characteristics but the bitumen prescreening tests results were the key in identifying optimum membranes for this application. The final selection of membranes was made by the scientific authority after an evaluation of the results had been made.

The three TFC membranes tested all exhibited very good TOC rejections of between 98 - 99%. The flux rate for the G10 membrane was initially lower than the other TFC membranes but showed virtually no decrease with time. Membrane G50 had a higher flux rate than the G10 but was decreasing at a slow but steady rate. Membrane G20 was initially higher than both the G10 and G50 membranes but by the end of 3 1/2 hours had decreased to below that for the other two membranes.

FIGURE 3 - 2

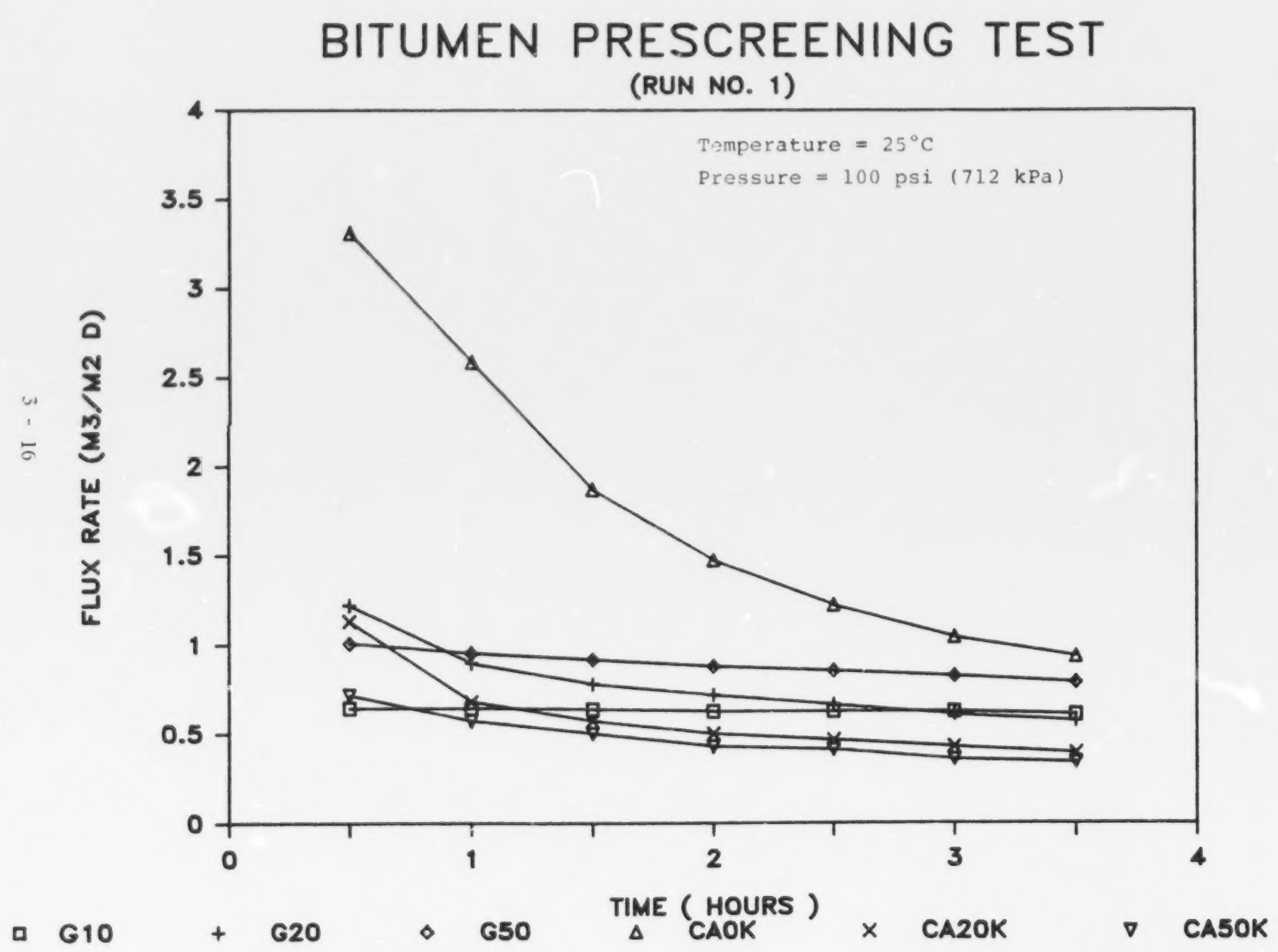

BITUMEN PRESCREENING TEST
(RUN NO. 1)
Temperature = 25°C
Pressure = 100 psi (712 kPa)
FLUX RATE (M3/M2 D)
TIME (HOURS)
0
0.5
1
1.5
2
2.5
3
3.5
4
G10
G20
G50
CA0K
CA20K
CA50K

FIGURE 3 - 3

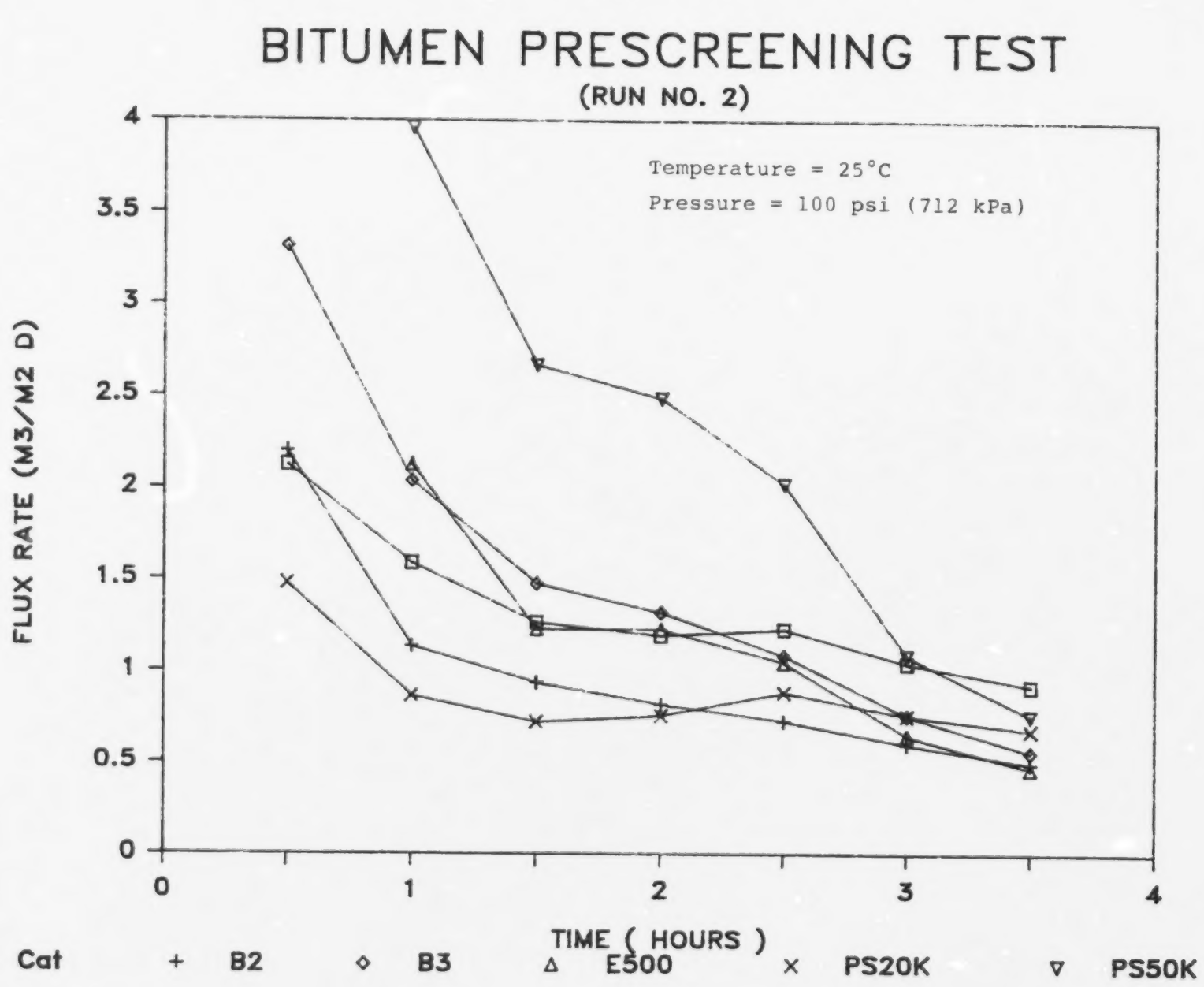

BITUMEN PRESCREENING TEST
(RUN NO. 2)
Temperature = 25°C
Pressure = 100 psi (712 kPa)
FLUX RATE (M3/M2 D)
TIME (HOURS)
0
0.5
1
1.5
2
2.5
3
3.5
4
Cat
B2
B3
E500
PS20K
PS50K

FIGURE 3 - 4

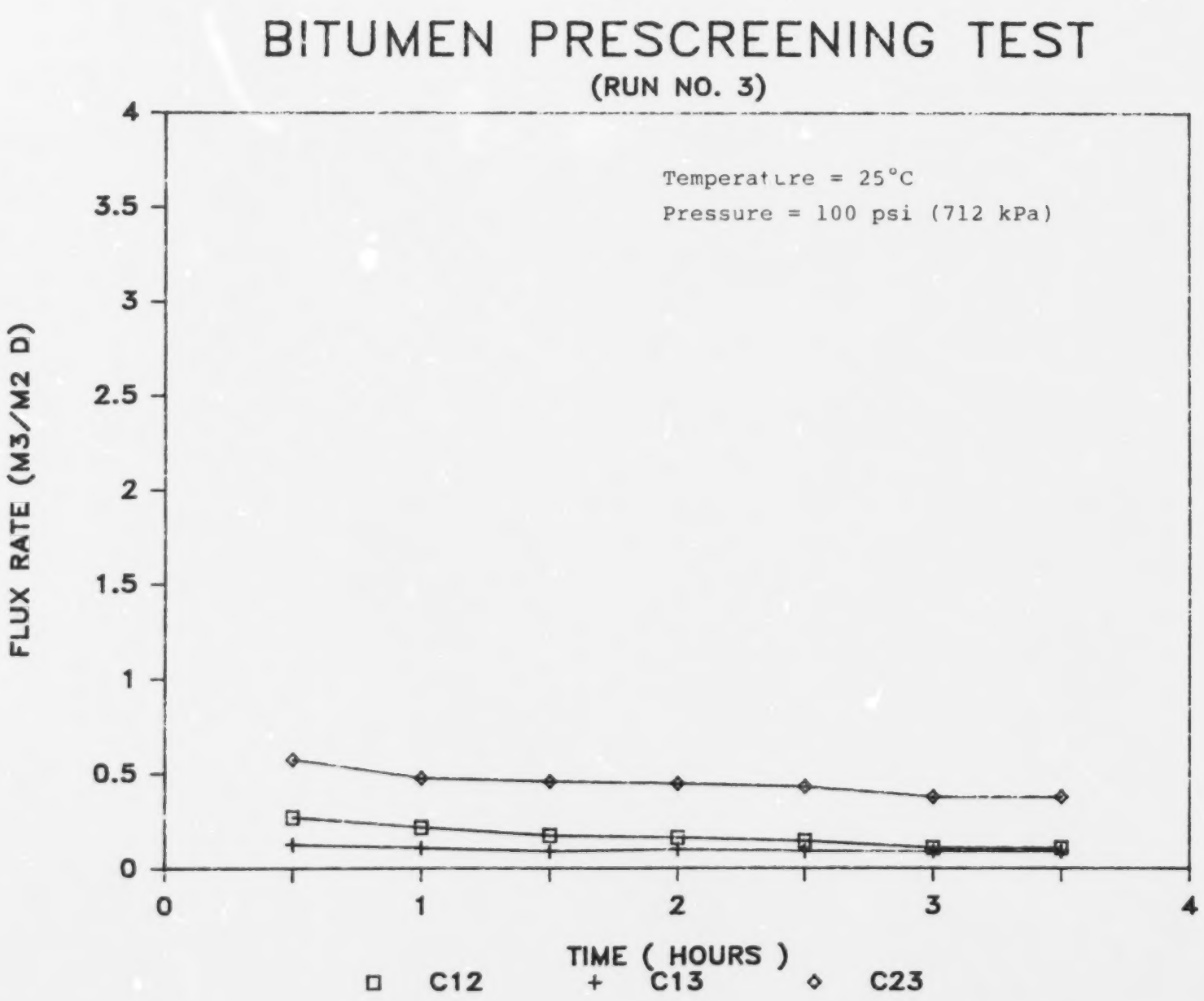

BITUMEN PRESCREENING TEST
(RUN NO. 3)
Temperature = 25°C
Pressure = 100 psi (712 kPa)
FLUX RATE (M3/M2 D)
4
3.5
3
2.5
2
1.5
1
0.5
0
0
1
2
3
4
TIME (HOURS)
C12
C13
C23

TABLE 3 - 7

MEMBRANE EFFICIENCY DURING
BITUMEN PRESCREENING TESTS

MEMBRANE	(AVERAGE) % REJECTION TOC	MEMBRANE	(AVERAGE) % REJECTION TOC
TFC G10	99.34	PS E500	96.82
TFC G20	97.94	PS 20K	94.34
TFC G50	98.17	PS 50K	96.87
CA 0K	96.17	CELLULOSE 12	91.78
CA 20K	93.66	CELLULOSE 13	88.33
CA 50K	93.66	CELLULOSE 23	94.77
CHP Cat	97.48		
CHP B2	48.43		
CHP B3	97.61		

Operating Temperature = 25 deg. C
Operating Pressure = 100 psi (712 KPa)

Based on the steady flux for G10 it was chosen as the best TFC membrane for further work.

The three cellulose acetate membranes, CA-0K, CA20K, and CA50K exhibited TOC rejections of 96%, 94%, and 94% respectively. The flux rate for CA-0K was initially high but decreased very rapidly during the 3 1/2 hour run. The flux rates for CA20K and CA50K were both low but relatively stable during the run. The CA20K membrane was chosen as a result of its stable flux.

CHP membranes Cat and B3 had rejections of TOC of 97.5% and 97.6%. The flux rate for B3 was initially very high but decreased rapidly during the test. The CHP-Cat membrane showed some fluctuation in flux rate but was relatively stable with time. The flux for Cat was consistently higher than that of B2. The rejection for CHP B2 was only 48.4%. The flux rate for CHP B2 declined steadily during the test. Cat was chosen as a result of its high stable flux and good rejection of TOC.

Polysulfone (PS) membranes E500, 20K, and 50K obtained TOC rejections of 96.8%, 94.3%, and 96.9% respectively. The flux rate for PS50K was initially very high but decreased rapidly over the 3 1/2 hours of the test. The E500 membrane had a high flux which gradually decreased during the test and the PS20K had a lower more stable flux. The E500 membrane was chosen over the PS20K membrane even though the flux rate of the PS20K was stable because of the more ready availability of the E500 membrane in a variety of configurations.

The three cellulose membranes C12, C13, and C23 had rejections of 91.8%, 88.3%, and 94.8% respectively. The flux rates for all three membranes were stable but low relative to the other

membranes. As a result of the low flux rates of all three cellulose membranes, they were dropped from the experimental program at this time. The cellulose membrane RC-51, which was not available at the time of the prescreening tests, was used to replace the other cellulose membranes.

The polyvinyl difluoride (PVDF) membrane was not tested because only one such membrane was available for testing.

3.2.4 Polyethelene Glycol (PEG) Test

The results of the PEG test were used to characterize the selected membranes with respect to their molecular weight cut offs. A summary of the results of the PEG test showing the percent rejection of TOC and the estimated molecular weight cut offs for the membranes is shown in Table 3-8. Appendix C contains the complete data for the test.

The molecular weight cut offs were estimated by comparing the percent rejection of TOC for each membrane with percent rejections of TOC for membranes of known molecular weight cut offs. Four of the membranes, CA-20K, PS-E500, CHP-CAT, and PVDF had percent rejections between 5% and 15% suggesting molecular weight cut offs between 15-20K. The TFC-G10 membrane and the Cellulose RC51 had much higher rejections of 82% and 88% suggesting molecular weight cut offs between 6-10K.

TABLE 3 - 8

ESTIMATED MOLECULAR WEIGHT CUT OFF
BASED ON THE PEG TEST

MEMBRANE	PEG % REJECTION OF TOC	ESTIMATED MOLECULAR WEIGHT CUT OFF
CA-S-20K	5%	15 - 20K
PS-E500	8%	15 - 20K
TFC-G10	82%	6 - 10K
CHP-Cat	13%	15 - 20K
C-RC51	88%	6 - 10K
PVDF	8%	15 - 20K

Operating Temperature = 25 deg. C
Operating Pressure = 100 psi (712 KPa)

3.3 Membrane Screening Tests

The flux rates for the eight screening test runs are shown in Figures 3-5 to 3-12. Complete results of the screening tests are presented in Appendix D.

The flux rates for the cellulose membrane during the first six runs were consistently very poor. During the seventh run the cellulose membrane was replaced with an additional sample of CHP membrane. The flux rates for the other membranes were similar during the runs but the cellulose acetate membrane tended to have slightly higher flux rates than the others. Of the remaining four membranes no one membrane in particular consistently out performed the others.

In order to evaluate whether temperature and pH had a significant effect on the flux rate for each membrane two statistical tests were applied to the results. The flux rate at a 20% volume reduction for each membrane during each run were tabulated. This data is presented in Table 3-9. A correlation test and a multiple linear regression were applied to the data for each membrane using temperature and pH as the independent variables and flux rate at 20% volume reduction as the dependent variable.

Table 3-10 shows the T-test results from the linear regression test for the pH and temperature coefficients. Complete results of the correlation test and multiple linear regression are presented in Appendix D. The higher the T-test result on a particular coefficient the greater the likelihood that the factor does have a significant effect. In order to have a 95% probability that a factor is significant with five degrees of freedom the T-test value must be

FIGURE 3 - 5

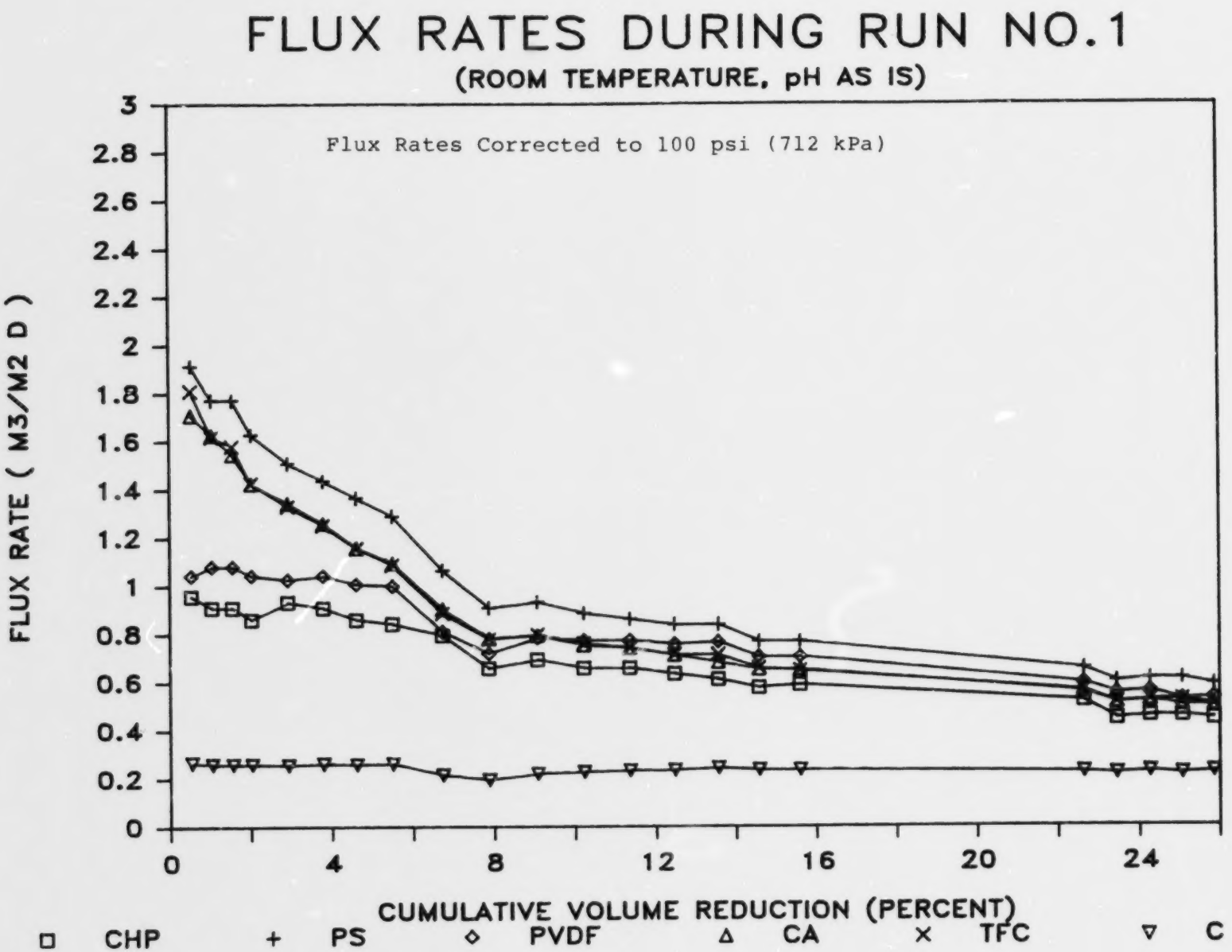

FLUX RATES DURING RUN NO.1
(ROOM TEMPERATURE, pH AS IS)
Flux Rates Corrected to 100 psi (712 kPa)
FLUX RATE (M3/M2 D)
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
4
8
12
16
20
24
CUMULATIVE VOLUME REDUCTION (PERCENT)
CHP
PS
PVDF
CA
TFC
C

FIGURE 3 - 6

FLUX RATE DURING RUN NO.2

(TEMPERATURE 45C / pH AS IS)

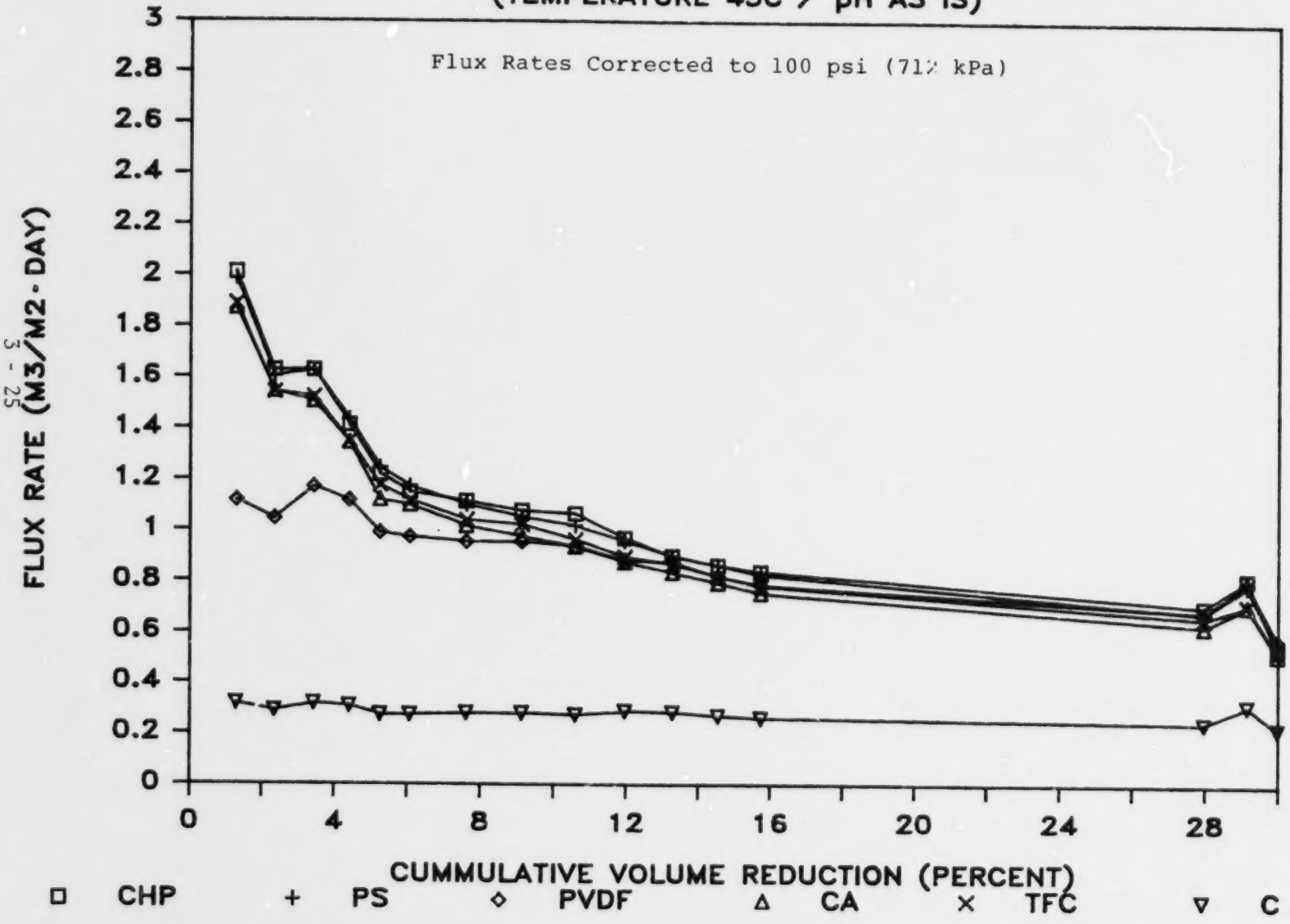


FIGURE 3 - 7

FLUX RATE DURING RUN NO.3

(ROOM TEMPERATURE, pH 5.5)

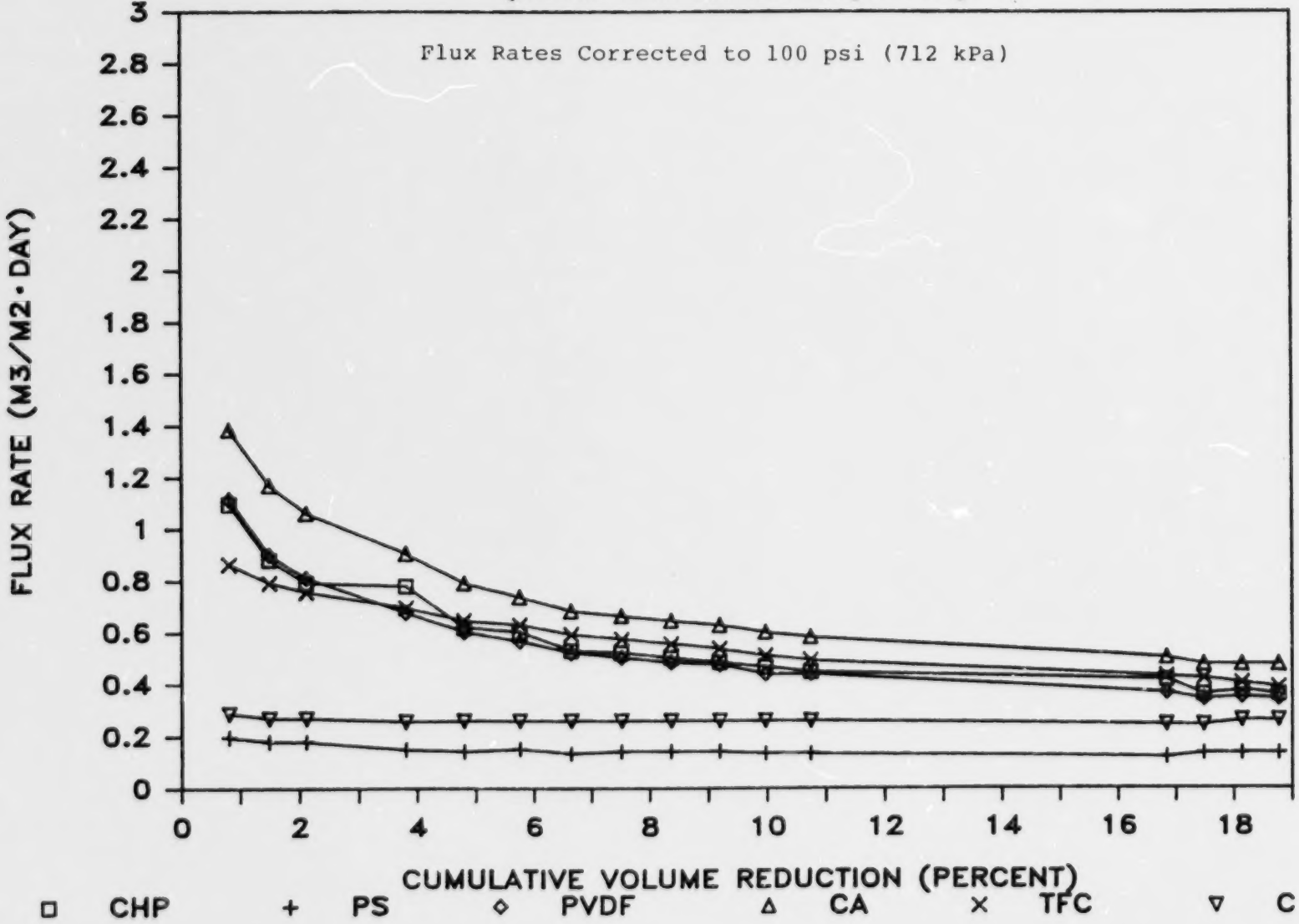


FIGURE 3 - 8

FLUX RATE DURING RUN NO.4

(TEMPERATURE 45C / pH 5.5)

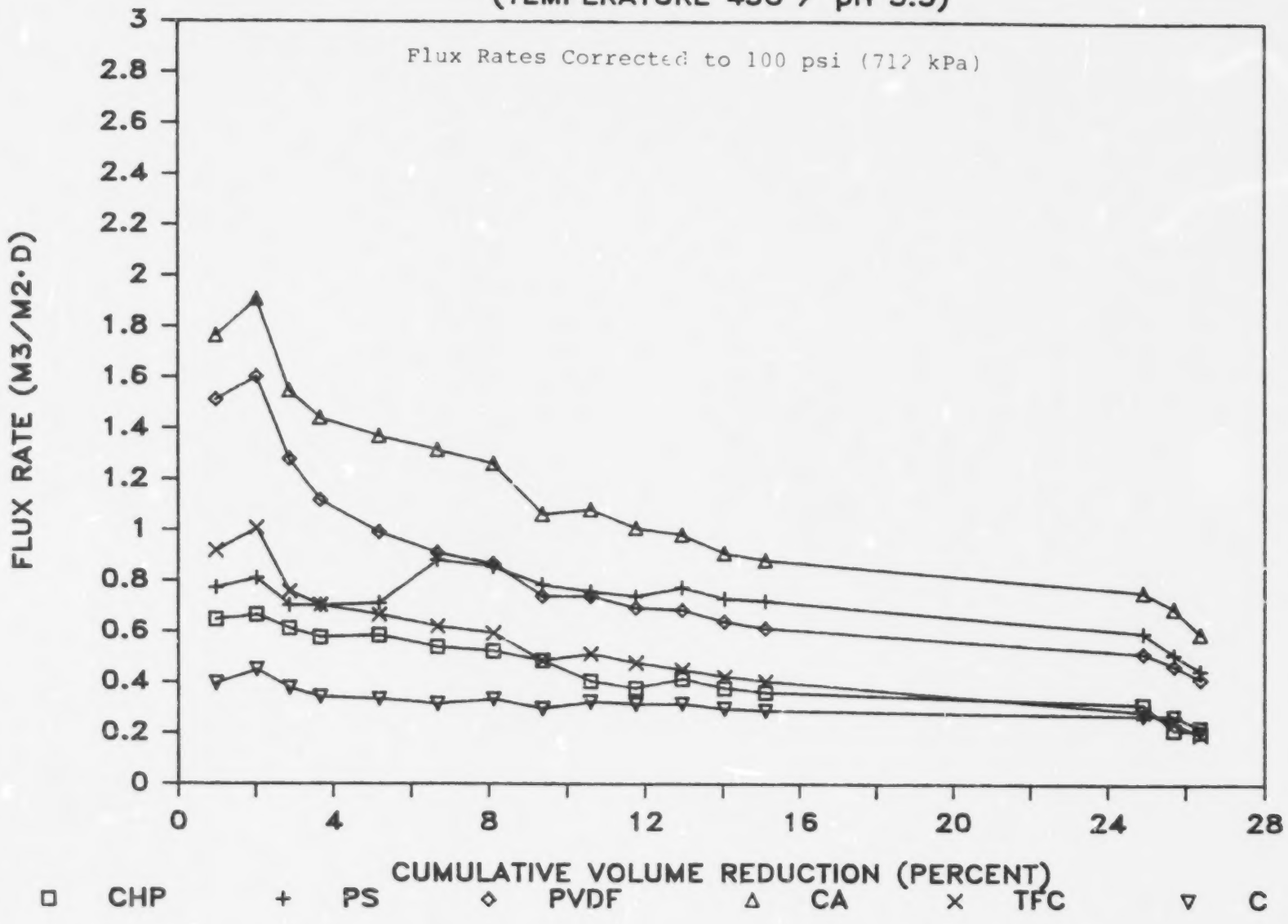


FIGURE 3 - 9

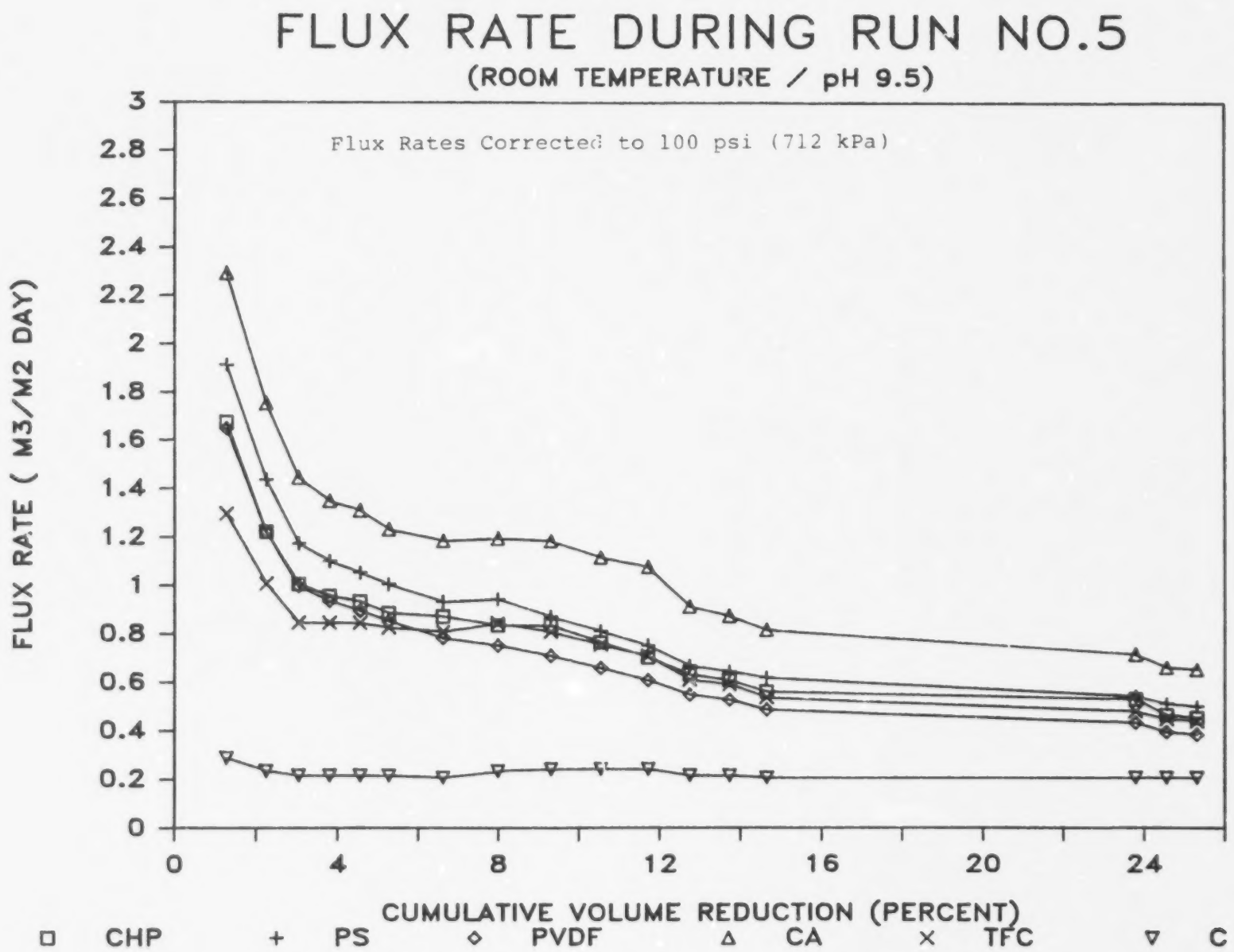

FLUX RATE DURING RUN NO.5
(ROOM TEMPERATURE / pH 9.5)
Flux Rates Corrected to 100 psi (712 kPa)
FLUX RATE (M3/M2 DAY)
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
4
8
12
16
20
24
CUMULATIVE VOLUME REDUCTION (PERCENT)
□ CHP
+ PS
◇ PVDF
△ CA
× TFC
▽ C

FIGURE 3 - 10

FLUX RATE DURING RUN NO.6

(TEMPERATURE 45 C / pH 9.5)

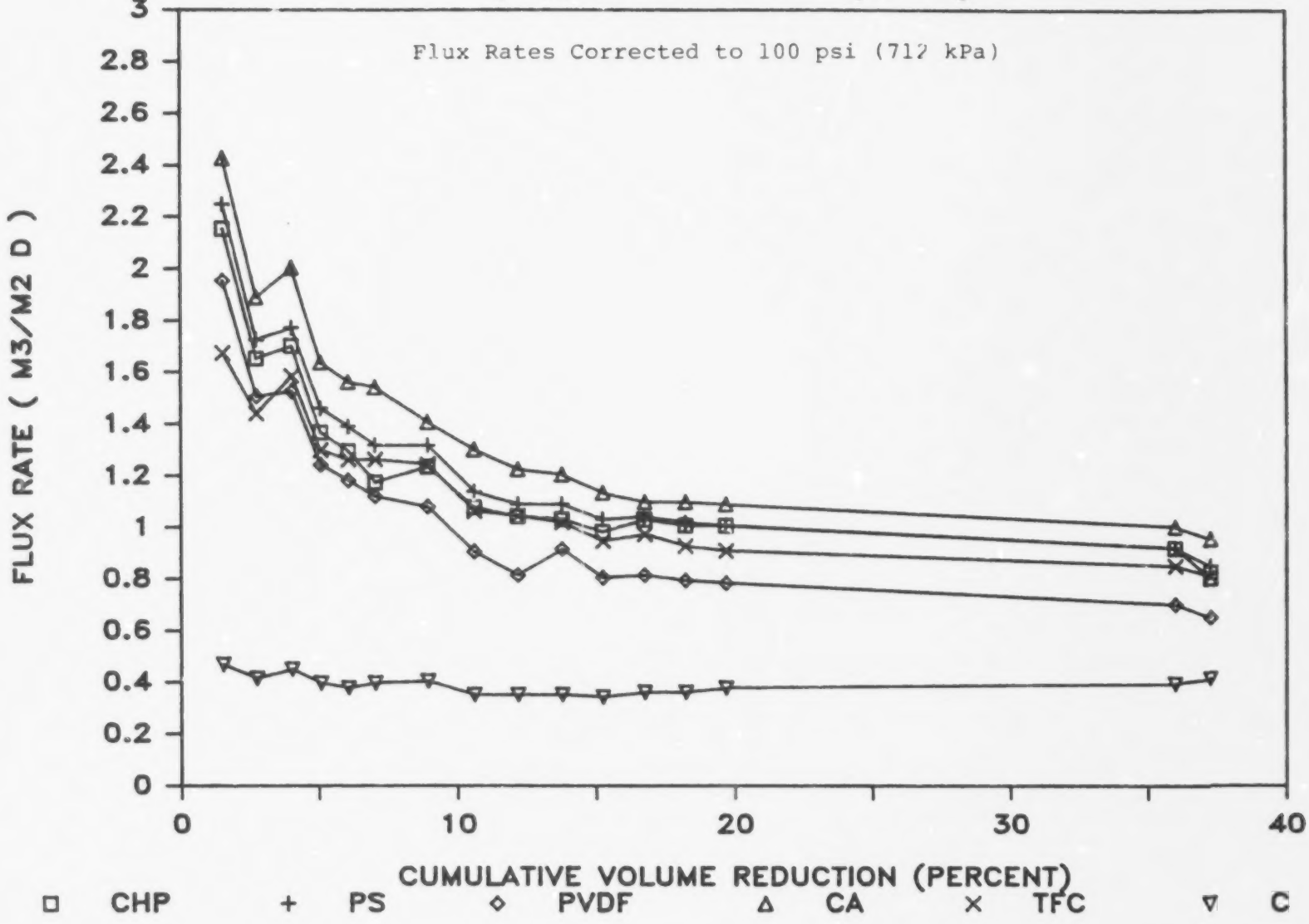


FIGURE 3 - 11

FLUX RATES DURING RUN NO.7

(TEMPERATURE 65 C / pH AS IS)

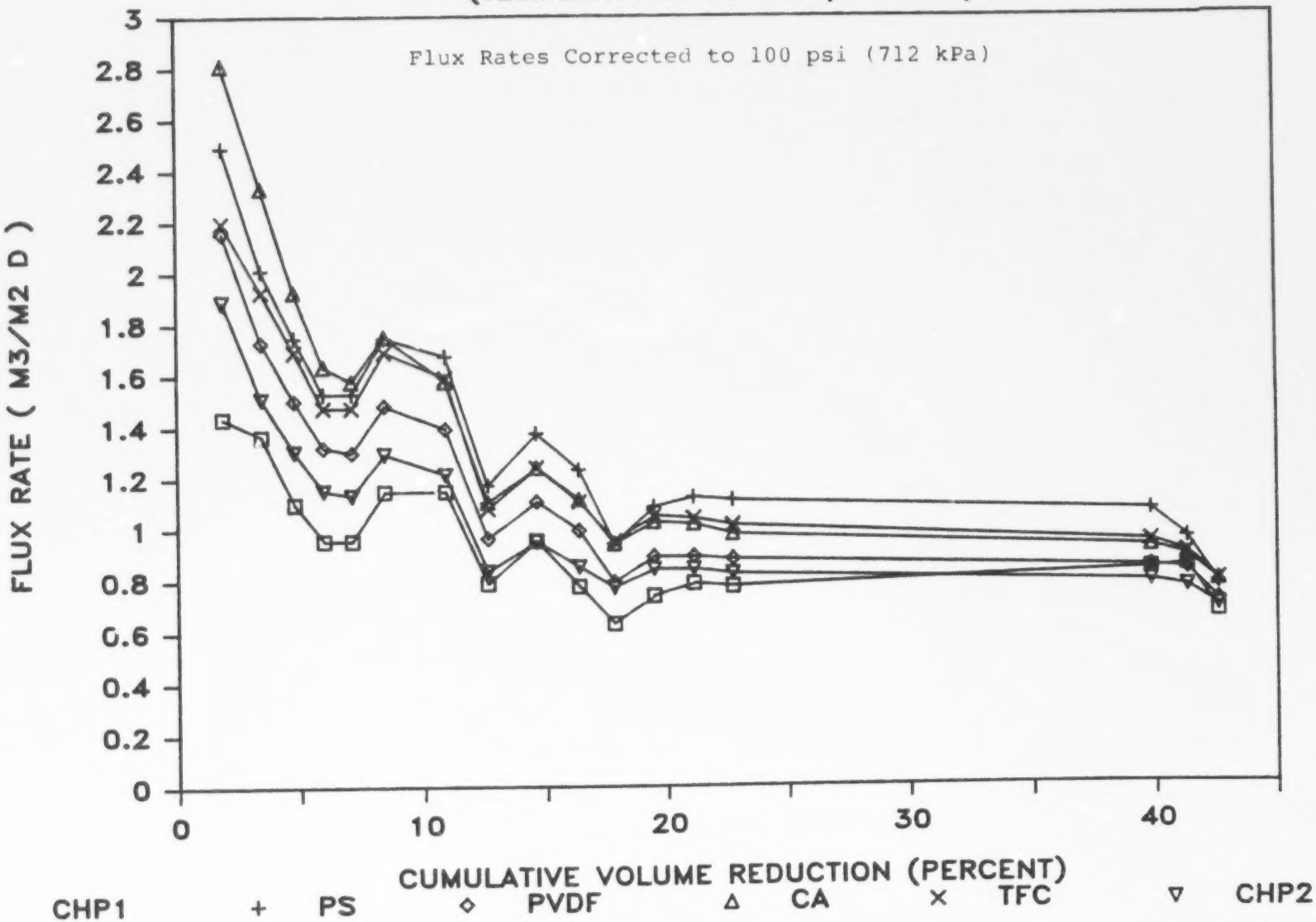


FIGURE 3 - 12

FLUX RATES DURING RUN NO.8

(TEMPERATURE 65 C / pH AS IS)

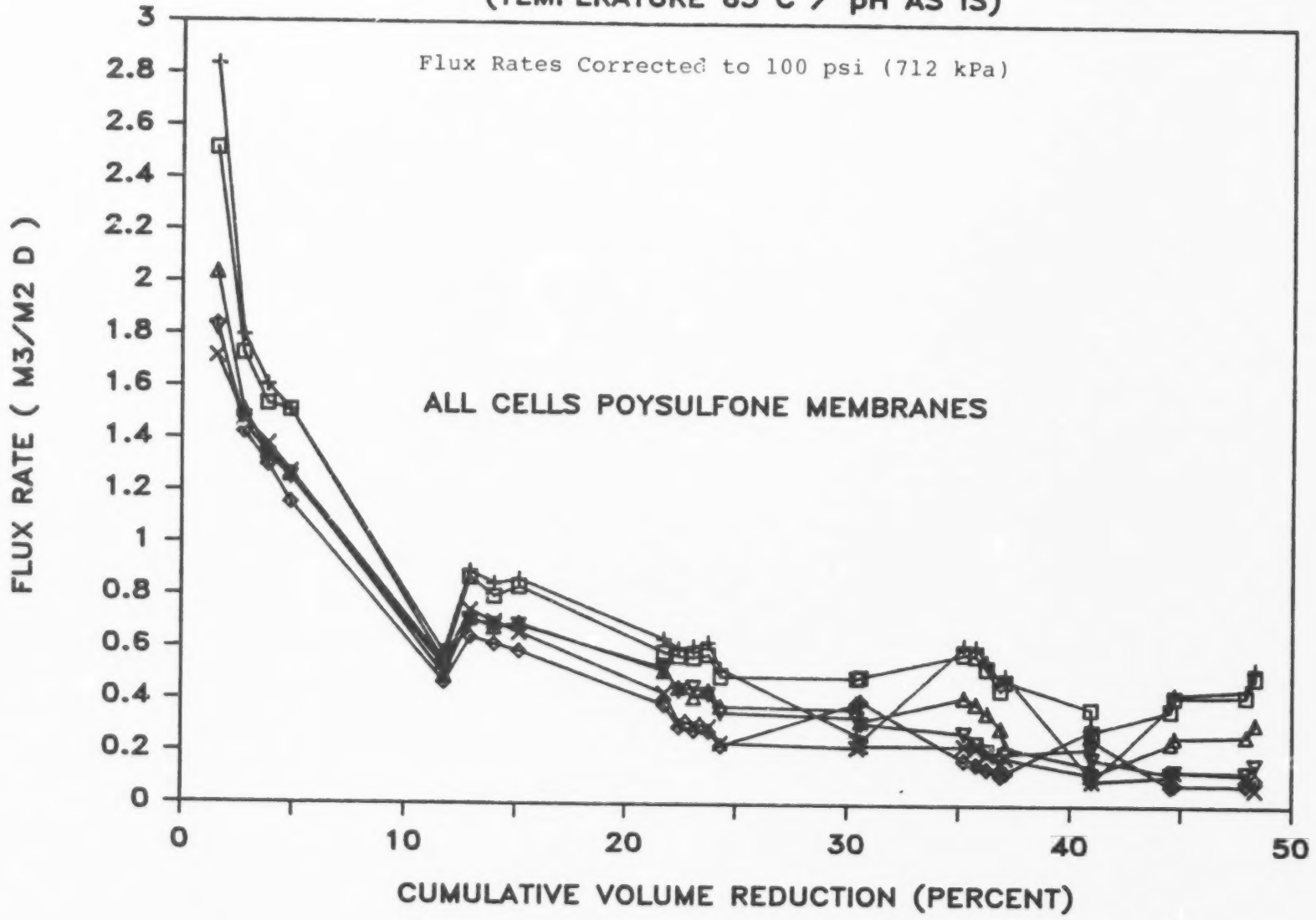


TABLE 3 - 9

FLUX RATES AT 20 % VOLUME REDUCTION

RUN NO.	CHP FLUX RATE M3/M2 D	PS FLUX RATE M3/M2 D	TFC FLUX RATE M3/M2 D	C FLUX RATE M3/M2 D	CA FLUX RATE M3/M2 D	PVDF FLUX RATE M3/M2 D
1	0.55	0.70	0.63	0.22	0.59	0.59
2	0.79	0.78	0.75	0.25	0.74	0.71
3	0.48	0.18	0.39	0.26	0.51	0.39
4	0.45	0.88	0.35	0.28	0.88	0.65
5	0.55	0.57	0.50	0.21	0.76	0.45
6	0.99	0.99	0.90	0.38	1.07	0.77
7	0.81	1.10	1.05	ND	1.03	0.89
MEAN	0.66	0.74	0.65	-	0.80	0.64

RUN 1 pH AS IS, ROOM TEMPERATURE (25C)
2 pH AS IS, TEMPERATURE (45C)
3 pH 5.5, ROOM TEMPERATURE (25C)
4 pH 5.5, TEMPERATURE (45C)
5 pH 9.5, ROOM TEMPERATURE (25C)
6 pH 9.5, TEMPERATURE (45C)
7 pH AS IS, TEMPERATURE (65C)

ND - not done

All Flux Rates are Pressure Corrected to 100 psi (712 KPa)

TABLE 3 - 10

SIGNIFICANCE TEST OF pH AND TEMPERATURE COEFFICIENTS
IN MULTIPLE LINEAR REGRESSION

MEMBRANE	T-TEST ON pH COEFFICIENT	T-TEST ON TEMP CEFFICIENT
CHP	2.34	2.28
PS	1.45	3.56
TFC	2.08	2.85
CA	2.03	3.82
PVDF	1.24	5.42
CELLULOSE	0.43	1.55

greater than 2.02. On this basis it is apparent that temperature does have a significant effect on the flux rates.

The cellulose T-test result for temperature is less significant partially because no run was conducted at 65°C with this membrane. Figure 3-13 shows the flux rates for each membrane during runs at different temperatures.

The results showed consistently positive correlation between flux rate and increasing pH. The T-test data also shows pH to be a significant factor in determining flux rate for some of the membranes. It is possible that by increasing the pH of the emulsion, the emulsion stability is enhanced, and membrane fouling tends to decrease. Although the increase in flux with increasing pH is not as significant as increases in flux with temperature its effect should be noted. Figure 3-14 shows the flux rates for each membrane at different pH values.

Table 3-11 shows a summary of the permeate qualities generated during the screening tests. This data shows generally poor rejection of components by the cellulose membrane, similar rejections by the CA, PS, CHP, and PVDF membranes, and generally better rejections by the TFC membrane.

Table 3-12 shows the range of percent rejections for different components obtained for each membrane during the first seven runs. The rejection of conductivity by the cellulose membrane was poor ranging between 0-14%. The CA, PS, CHP and PVDF membranes were better with rejections ranging between 25-53%, 31-65%, 33-68%, and 36-58% respectively. The TFC membrane was still better with percent rejections between 63-81%. No trends in rejection of conductivity

FIGURE 3 - 13

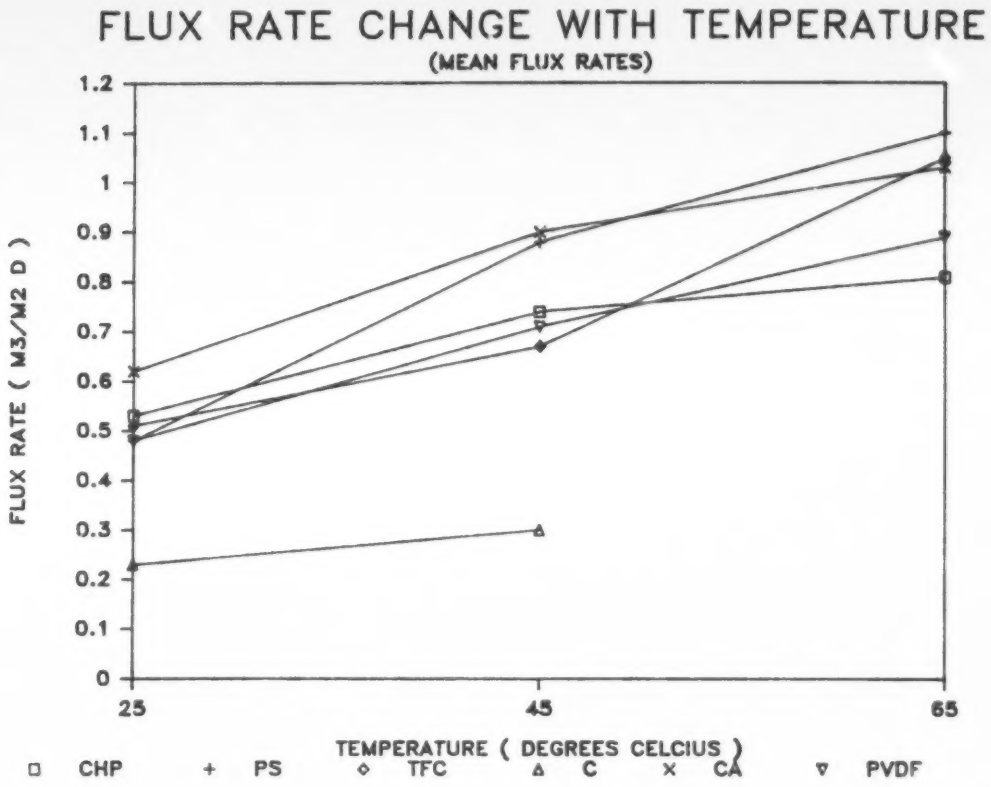


FIGURE 3 - 14

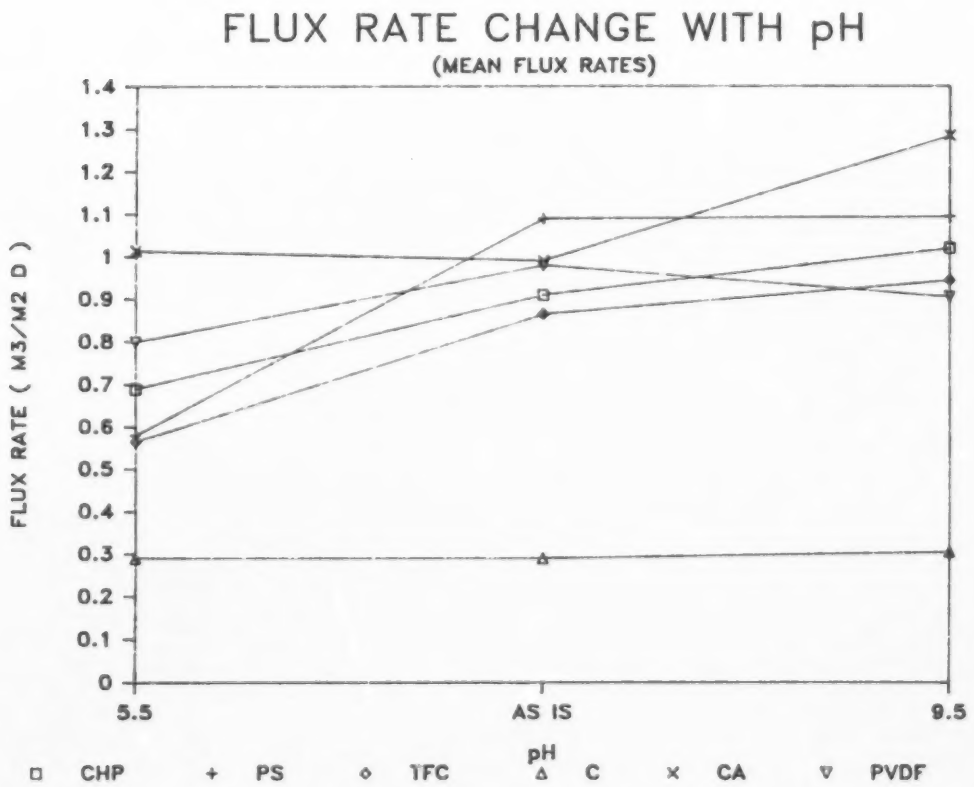


TABLE 3 - 11

PERMEATE QUALITY DURING SCREENING TESTS

	CONDUCTIVITY (uHmos)	TURBIDITY (NTU)	TOC (mg/L)	TDS (mg/L)	HARDNESS (mg/L)	SILICA (mg/L)
FEED	913 - 1210	1090 - 2410	1025 - 2919	980 - 1155	3.1 - 36.1	61 - 85
PERMEATES						
CELLULOSE	850 - 1075	0.8 - 1.2	42 - 140	605 - 845	0.6 - 28	40 - 69
CA	470 - 800	0.4 - 0.9	32 - 88	308 - 561	<0.15 - 7.2	41 - 70
PS	385 - 630	0.4 - 2.2	32 - 66	399 - 475	<0.15 - 8.7	36 - 70
CHP	358 - 640	0.4 - 0.9	21 - 76	362 - 470	<0.15 - 4.5	39 - 68
PVDF	420 - 590	0.3 - 0.7	22 - 67	325 - 430	<0.15 - 4.2	39 - 71
TFC	195 - 375	0.1 - 0.4	8 - 45	160 - 262	<0.15 - 0.75	40 - 64

TABLE 3 - 12

PERCENT REJECTIONS OF DIFFERENT COMPONENTS
DURING MEMBRANE TESTS

	PERCENT REJECTION				
MEMBRANE	CONDUCTIVITY	TOC	TDS	HARDNESS	SiO2
CELLULOSE	0 - 14	91 - 96	19 - 44	23 - 86	19 - 43
CA	25 - 53	94 - 98	43 - 73	67 - 99	18 - 39
PS	31 - 65	95 - 98	51 - 64	82 - 99	18 - 42
CHP	33 - 68	94 - 98	52 - 68	81 - 99	20 - 42
PVDF	36 - 58	96 - 98	59 - 70	84 - 99	16 -44
TFC	63 - 81	97 - 98	74 - 86	98 - 99	18 - 42

with respect to pH and temperature were observed. All membranes were able to reject virtually all (99.9%) of the turbidity present in the feed. During the eight runs the turbidities of the permeates for all membranes were less than 1 NTU. All membranes rejected virtually all the emulsified oil present in the feed.

The TOC rejections for all membranes were quite high but rejections for the cellulose were generally lower and the rejections for the TFC somewhat higher than for the other membranes. No definite trends for rejection of TOC with respect to temperature were observed but the two lower pH runs tended to have slightly poorer rejections. The rejections of TDS were lowest (19-44%) for the cellulose membrane and highest (74-86%) for the TFC membrane. The others all had rejections between 43-73%. No trends for TDS rejection with respect to pH and temperature were observed.

Rejection of hardness followed a similar pattern as for other components. Rejection were lowest (0-86%) for cellulose and highest (98-99%) for TFC. The high rejections of hardness by the TFC membrane would reduce the load on downstream softening processes in produced water treatment systems. The rejections for CA were slightly lower, 67-99%, than for the PS, CHP and PVDF membranes which ranged from 81-99%. The level of hardness present in the feed increased when the pH of the feed was lowered. The rejection of hardness was also poorer at a pH of 5.5.

The rejections of dissolved silica were very similar for all the membranes ranging from the high teens to the low forties. No trends in the rejection of silica were observed with respect to temperature or pH.

The GC and IR analysis conducted on the permeate from run eight showed naphthenic acids to be present at a concentration of about 7 mg/L. The presence of soluble organic material such as naphthenic acid is not a problem for boiler feeds when, as the results demonstrated, essentially all oil is removed.

Based on the results of these screening tests and discussion with the Scientific Authority three membranes; TFC, PS, and CHP were chosen as the best membranes for further work. The TFC had by far the best rejections of contaminants in the emulsion and maintained a stable and relatively high flux (0.65 m^3/m^2 D mean). The PS membrane had rejections similar to CHP and PVDF membranes and maintained the highest flux (0.74 m^3/m^2 D mean) of the three. The PS membrane is also considerably less expensive than the TFC membrane. The CHP membrane was included because its rejections were good and it maintained a flux rate slightly higher than the PVDF.

The CA membrane maintained the best flux rate of all the membranes (0.80 m^3/m^2 D mean) but had consistently lower rejections of various contaminants than the CHP, PS, TFC, and PVDF membranes. The flux rates and rejection for the cellulose membrane was consistently very poor during the tests.

The results also demonstrated that the operating temperature should be as high as possible in order to maximize the flux rate through the membrane. Temperature appeared to have no impact on the ability of membranes to reject emulsion components.

Increases in pH appeared to have a positive impact on the flux rate of the membranes. Low pH also had a detrimental effect on the removal of hardness by the membranes. If the pH of the water

being treated is to have its pH adjusted upwards at some point such as is required for industrial boiler feedwater treatment process it may be desirable to make this upward adjustment before the membrane processing step.

3.4 Batch Concentration Test

The flux rate data for the batch concentration test are shown in Table 3-13 and in Figure 3-15. Results from analyses of samples taken during the run are presented in Table 3-14. Complete results are included in Appendix E.

The results showed a rapid drop in flux rate for all three membranes as the cumulative volume reduction increased from 0 to 30%. The flux rates for PS and TFC were stable between 30% and 80% volume reduction near 0.50 and 0.32 m^3/m^2 D respectively. The flux rate for CHP decreased slowly from 0.76 to 0.5 m^3/m^2 D during this time. The flux rates for all three membranes decreased rapidly between 80% and 90% volume reduction. During this period of time the temperature of the emulsion feed which had been stable between 60°C and 65°C decreased to 55°C. The increasing concentration of bitumen in the feed may be partially responsible for the drop in flux rate but the decrease in temperature was likely a significant factor as well.

During the test no sign of any change in emulsion stability was observed. At a 90% volume reduction a sample of the concentrate did not separate even after standing for several hours.

The analytical data from the test demonstrate that the TFC membrane is significantly more efficient in removing TOC than the CHP or PS membranes. At a 90% volume reduction the concentrations of TOC

TABLE 3 - 13

FLUX RATES DURING BATCH CONCENTRATION TEST

TIME (MIN)	CHP FLUX RATE (M3/M2 D)	TFC FLUX RATE (M3/M2 D)	PS FLUX RATE (M3/M2 D)	% VOLUME REDUCTION
0.0				
60.0	3.40	1.40	2.25	2.27
220.2	2.36	1.89	1.95	8.14
1020.0	1.01	0.88	0.83	19.87
1080.0	0.76	0.52	0.35	31.09
1140.0	0.68	0.52	0.37	32.02
1200.0	0.83	0.56	0.39	37.49
1320.0	0.71	0.53	0.34	47.52
1380.0	0.61	0.50	0.33	52.20
1440.0	0.61	0.50	0.31	56.82
1500.0	0.63	0.47	0.31	60.27
2460.0	0.56	0.48	0.30	67.12
2520.0	0.54	0.52	0.33	72.16
2580.0	0.52	0.54	0.33	77.26
2640.0	0.49	0.50	0.31	88.16
2760.0	0.27	0.27	0.15	88.80
2820.0	0.11	0.11	0.06	90.10

Operating Temperature = 65 deg. C
Operating Pressure = 100 psi (712 KPa)

FIGURE 3 - 15

FLUX RATE DURING BATCH CONCENTRATION

(TEMPERATURE 65 C / pH AS IS)

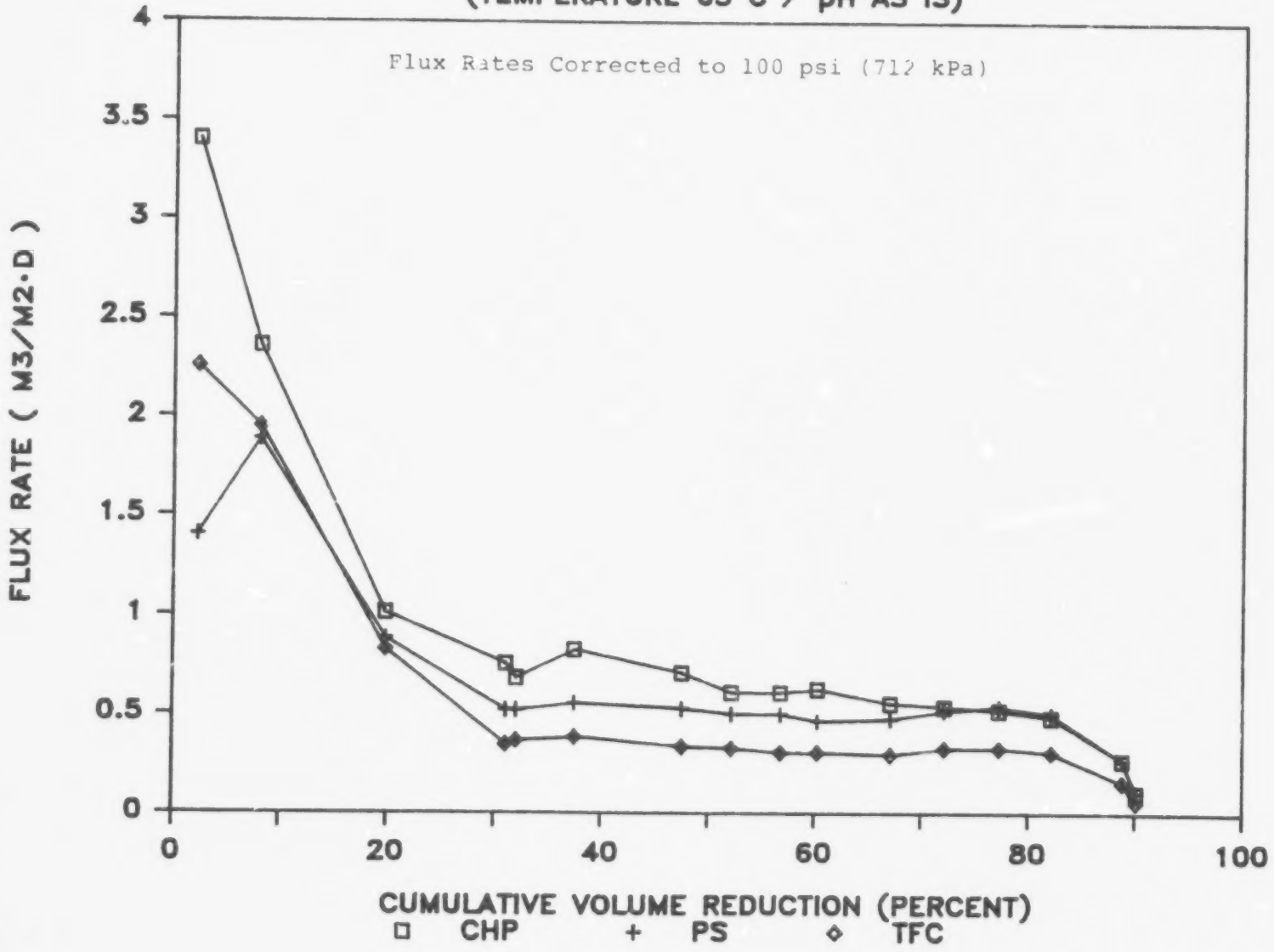


TABLE 3 - 14

BATCH CONCENTRATION RUN ANALYTICAL DATA

PARAMETER	UNIT	FEED	PERMEATE AT 30 % VOLUME REDUCTION			PERMEATE AT 60 % VOLUME REDUCTION			PERMEATE AT 90 % VOLUME REDUCTION		
			CHP	TFC	PS	CHP	TFC	PS	CHP	TFC	PS
TURB	NTU	1000	2.70	0.73	0.89	1.60	0.56	0.88	3.50	0.80	NA
TOC	mg/L	800	83.0	32.5	64.0	85.5	35.5	77.0	172.0	69.0	127.0
ALKALINITY	mg/L	NA	NA	NA	NA	NA	NA	NA	240	190	237

NO EMULSION BREAKING WAS OBSERVED EVEN AT 90% VOLUME REDUCTION

NA - data not available

in the permeates of CHP, TFC, and PS were 172 mg/L, 69 mg/L, and 127 mg/L respectively. The concentration of TOC in the permeates of all membranes increased as the feed became more concentrated.

3.5 Long Term Stability Test

The flux rate data for the long term stability test are shown in Figure 3-16. Results from analyses of samples taken during the run are presented in Table 3-15. Complete results are included in Appendix E.

This run was conducted as a continuation of the batch concentration run. A volume reduction of 90% was achieved after 47 hours of operation and from then on the permeates were recycled back to the process tank. The flux rates during the period between 47 and 70 hours were very low. The temperature and flow to the cells during this period of time were both lower than normal. The temperature during this period dropped from 65°C to 55°C and the flow to the cells dropped from 2 L/min to 1.2 L/min. When the temperature and flow to the cells were increased once again to their target values of 65°C and 2 L/min the flux rates for all three membranes increased as well. The flux rates for CHP, PS, and TFC reached values of 0.49, 0.47, and 0.24 m^3/m^2 D respectively. During the following 260 hours the CHP membrane consistently had the highest flux rate and exhibited only a moderate decline with time. The PS membrane started out almost as high as the CHP but exhibited a steeper flux rate decline over the period of the run. The TFC membrane had a lower flux at the start of the 90% reduction stability run than the CHP or PS membranes but had a very stable flux rate. By the end of the run the flux rate for PS had

FIGURE 3 - 16

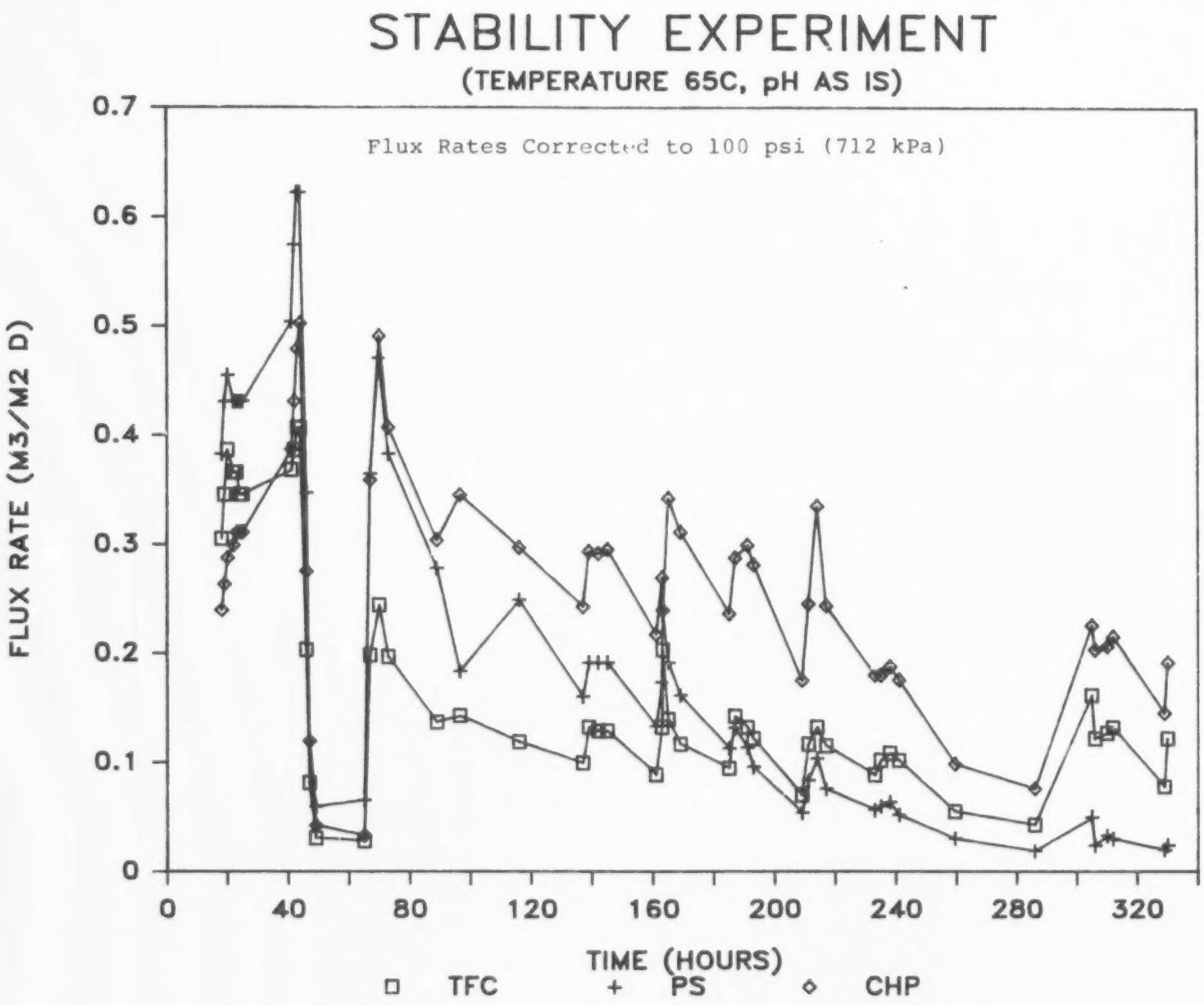

STABILITY EXPERIMENT
(TEMPERATURE 65C, pH AS IS)
Flux Rates Corrected to 100 psi (712 kPa)
FLUX RATE (M3/M2 D)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
40
80
120
160
200
240
280
320
TIME (HOURS)
TFC
PS
CHP

TABLE 3 - 15

LONG TERM STABILITY RUN ANALYTICAL DATA

PARAMETER	UNITS	CONCENTRATE				PERMEATES									ONCE THROUGH BOILER FEED QUALITY
						ONE DAY			ONE WEEK			TWO WEEK			
		FEED	1 DAY	1WEEK	2WEEK	CHP	TFC	PS	CHP	TFC	PS	CHP	TFC	PS	
pH		7.97	8.83	9.01	8.95	8.28	8.25	8.45	8.8	8.65	8.76	8.58	8.55	8.6	NS
COND	uHmos/cm	930	1100	3500	3800	750	440	620	2100	1750	2300	2500	2400	3250	NS
TURB	NTU	1000	7300	44000	17000	7.2	0.6	1.2	2.0	3.4	2.0	2.8	3.1	NA	NS
TOC	mg/L	880	1370	10100	7040	83	41	78	166	137	280	178	163	280	NS
TDS	mg/L	1117	1562	19964	11440	728	462	606	2516	1592	2640	1860	1300	2580	< 8,000
TSO	mg/L	1127	3222	6674	1517	NA	NA	NA	NA	NA	NA	NA	NA	NA	< 1.0
TSS	mg/L	44	125	1720	425	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.0
DIS SIO2	mg/L	84	112	NA	NA	69.4	61.5	64.0	62.2	67.2	73.2	32.7	40.0	40.2	< 50-150
HARDNESS	mg/L	12.0	72.0	211.0	133.0	116.0	0.4	0.6	3.6	3.3	6.0	2.9	1.8	7.4	< 0.5

NS - not specified
NA - analysis not done (TSO & TSS essencially zero for permeates)

decreased to be significantly less than that for the TFC membrane. Least square analysis of the flux rate data from 80 hours to the end of the run gives flux rate declines for CHP, PS, and TFC of 0.016, 0.024, and 0.003 m^3/m^2 D per day respectively. The high and relatively stable flux for the CHP membrane makes it an attractive membrane for further investigation.

As expected the analytical data for the long term stability runs show the best rejections for all components by the TFC membrane and similar rejections for the CHP and PS membranes. There appears also to be no significant decrease in rejection over time for any of the membranes.

The analysis of the concentrated emulsion in the process tank after one week and after two weeks shows a significant decrease in almost all components with time. Suspended oil and suspended solids decreased 77% and 75% respectively during the second week of operation. The concentration of all components except conductivity decreased. It was observed after the run that significant quantities of bitumen had coated most of the piping in the system and the pump internals. Since the total volume of concentrated emulsion was low, only about 4 liters, it is possible that oil and suspended solids were being lost to the inner surface of the system piping. The decrease in TSO during the second week of operation can be explained by only 20 grams of bitumen sticking to the piping.

During the run several attempts were made to clean the membranes by increasing the flow to the cells for short periods of time. After such flushing, the flux rates for all membranes increased slightly but only for a short period of time.

3.6 Reverse Osmosis Tests

3.6.1 RO Screening Test

Results of the RO membrane screening test using PS-UF membrane permeate as a feed are shown in Figure 3-17. Appendix F contains complete data for this test including data from the pre and post salt water flux test.

During the 4 1/2 hour initial salt water test the flux rates for the thin film composite (TFC) and cellulose acetate (CA) membranes decreased from 1.76 to 0.96 and from 1.41 to 0.69 m^3/m^2 D respectively. The rejections of conductivity for TFC and CA membranes were 97.4% and 96.3%.

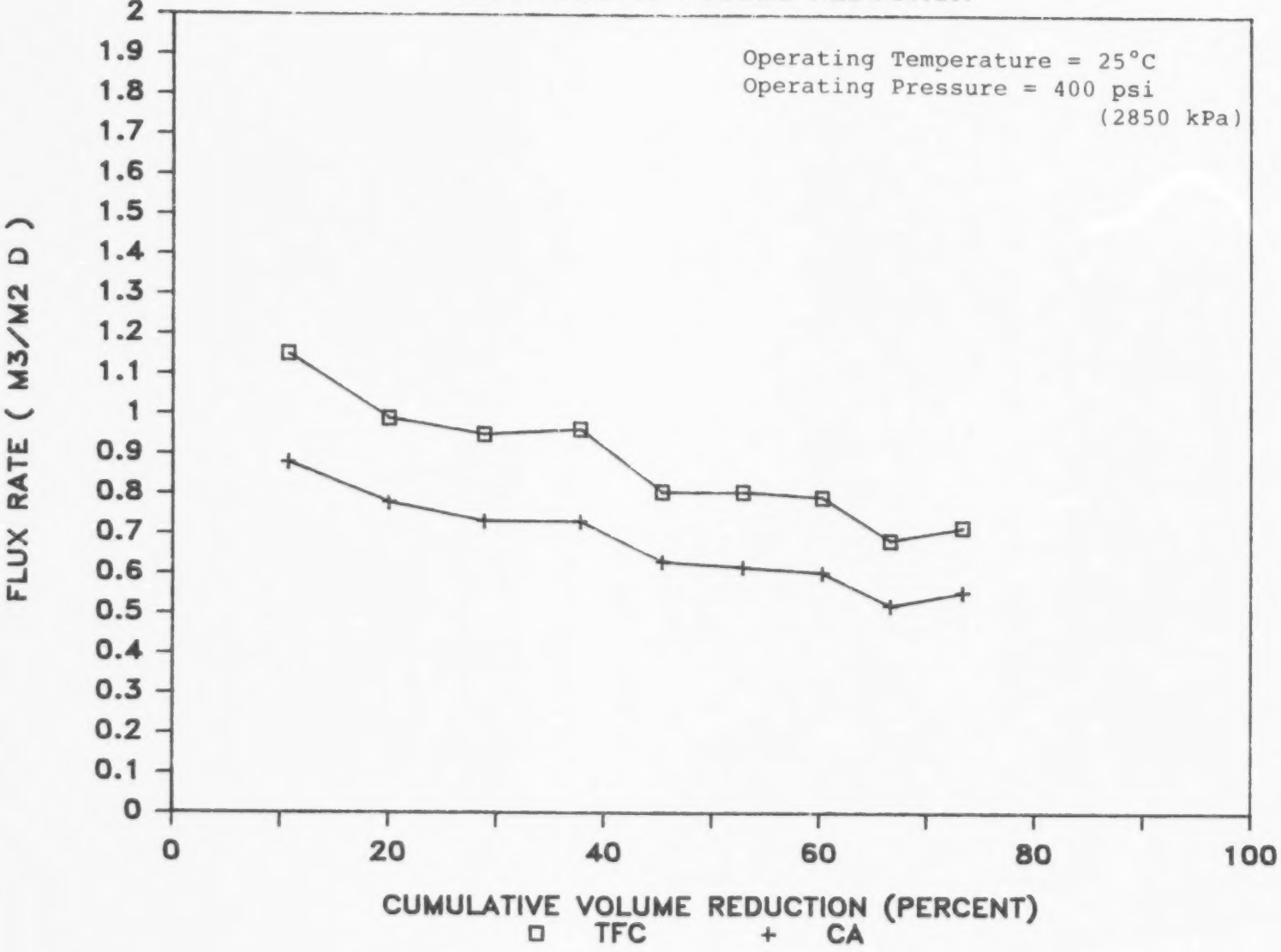
The system was then operated with UF permeate from a polysulphone (PS) membrane which had been operated with a feed of bitumen emulsion. During the 4 1/2 hours of this test the flux rates for TFC and CA membranes decreased from 1.15 to 0.72 and from 0.88 to 0.555 m^3/m^2 D respectively. The volume of feed was reduced by 73% during this time. The rejections of conductivity for the TFC and CA membranes were 98.6% and 97.8%. Also during the run the pH of the feed being concentrated increased from 8.2 to 8.5 and the pH of both the permeates decreased over the period of the run from about 7.1 to 6.5.

The flux rates for both membranes were relatively stable during the final salt water flux test. Flux rates during the 4 1/2 hour test for TFC and CA membranes went from 0.93 to 1.04 and from 0.755 to 0.69 m^3/m^2 D respectively. Rejections of conductivity were 97.7% and 94.9% for TFC and CA.

FIGURE 3 - 17

RO MEMBRANE SELECTION

FLUX RATE VS VOLUME REDUCTION



The TFC membrane had flux rates and conductivity rejections consistently better than the CA membrane. The decreases in flux during the initial salt tests are believed to be primarily the result of membrane compaction. The decrease in flux during the UF permeate run is believed to be the result of membrane compaction and a steadly increasing concentration of components in the feed.

Based on the results of this test the TFC membrane was chosen for use in further studies on RO treatment for final polishing of produced water.

3.6.2 Reverse Osmosis Test on Ultrafiltration Permeate

Flux rate data for the test of the TFC-RO membrane using TFC-UF membrane permeate as a feed are shown in Figure 3-18. Table 3-16 shows the results of analysis of the feed and of permeate samples taken during the test. Complete test results including salt water flux test data are presented in Appendix F.

The flux rate for the two hour initial salt water flux test started at 1.38 m^3/m^2 D, rose to 2.27 m^3/m^2 D after 45 minutes, then decreased to 1.22 m^3/m^2 D by the end of the run. The mean conductivity rejection during the test was 97.6%.

The RO system was then fed with permeate generated during a run using a UF TFC membrane, G10, with a feed of bitumen emulsion. During this run the flux rate through the RO TFC membrane was relatively steady at 1.35 m^3/m^2 D until the very end of the run when the flux rate dropped to 0.99 m^3/m^2 D. The volume reduction at the end of the run was 91% (concentration factor 11.1). The average rejection of conductivity during the run was 99.0%. The pH of the

FIGURE 3 - 18

RO TREATMENT OF UF PERMEATE

TFC FLUX RATE VS VOLUME REDUCTION

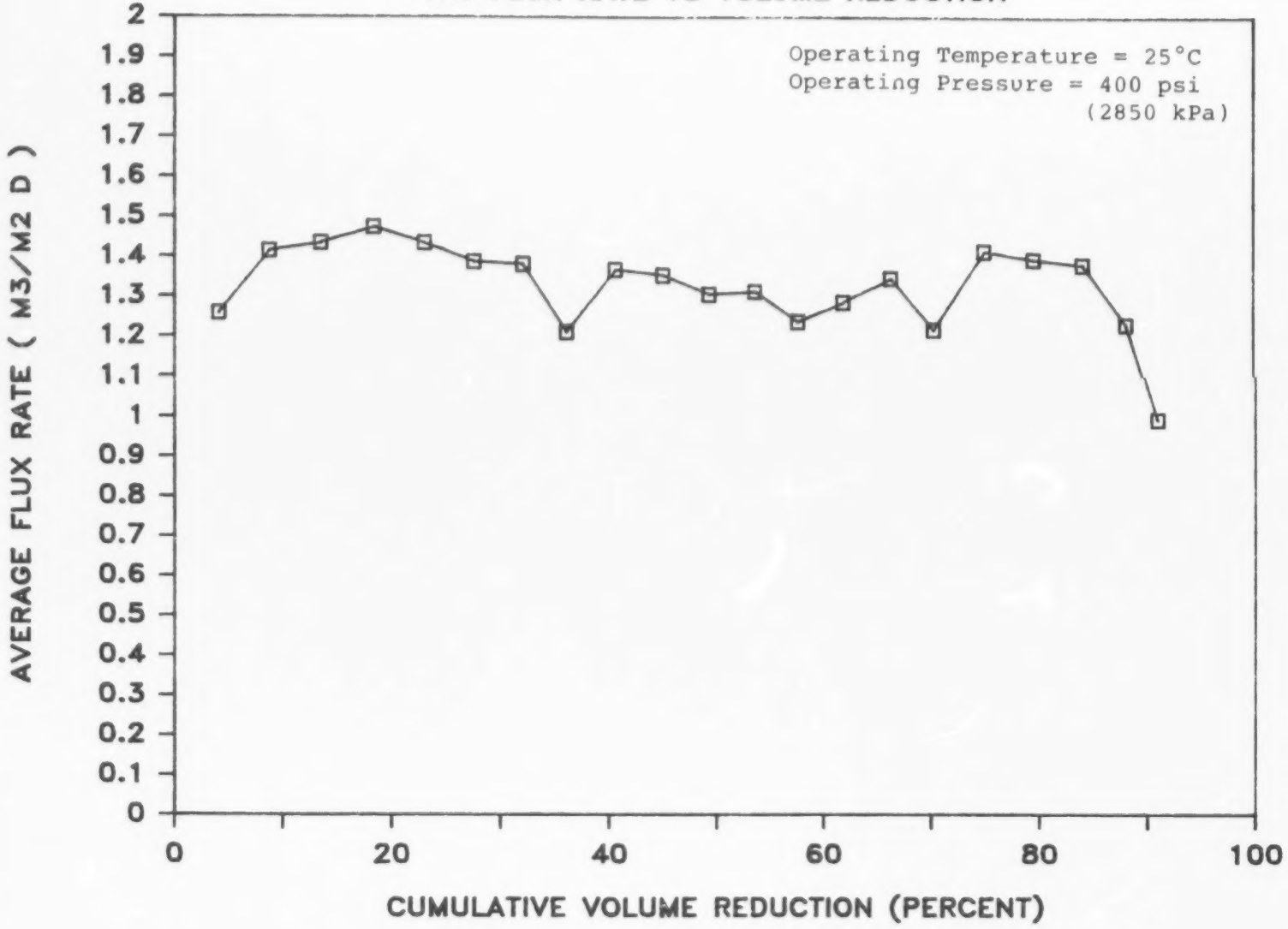


TABLE 3 - 16

ANALYTICAL DATA FOR RO TREATMENT OF UF PERMEATE

PARAMETER	UNITS	CONCENTRATE		PERMEATE			
		FEED	FINAL	30 MIN	30%	60%	91%
pH		8.55	8.60	6.00	6.17	6.08	6.60
COND	uHmos/cm	1100	2900	13	12	13	27
TURB	NTU	0.75	6.00	0.05	0.07	0.09	0.35
TOC	mg/L	75	122	10.2	4.5	1.5	1
TDS	mg/L	880	2630	<1	<1	20	30
HARDNESS	mg/L	2.82	16.78	0.79	0.83	0.50	0.29
DIS SIO2	mg/L	63.03	120.87	1.60	1.74	1.95	3.85
F	mg/L	5.20	17.80	0.03	0.03	0.04	0.09
Cl	mg/L	260.0	660.0	1.74	0.87	1.82	5.20
NO2	mg/L	<1	<1	<.1	<.1	<.1	<.4
PO4	mg/L	<0.1	<0.1	<.01	<.01	<.01	<.01
NO3	mg/L	<.04	<.04	<.04	<.04	<.04	<.04
SO4	mg/L	36.00	76.00	0.09	0.15	0.18	0.13
Be	mg/L	<.005	<.005	<.005	<.005	<.005	<.005
Mo	mg/L	0.020	0.070	<.005	<.005	<.005	<.005
Ca	mg/L	0.90	5.30	0.20	0.25	0.15	0.10
V	mg/L	<.005	0.015	<.005	<.005	<.005	<.005
Al	mg/L	0.05	0.17	<.01	0.01	<.01	0.01
Mg	mg/L	0.14	0.86	0.07	0.05	0.03	0.01
Ba	mg/L	<.005	0.015	0.005	<.005	<.005	<.005
K	mg/L	7.80	24.00	0.04	0.10	0.14	0.16
Sr	mg/L	0.005	0.020	<.005	<.005	<.005	<.005
Na	mg/L	280.0	800.0	2.4	1.7	2.3	6.1
Zn	mg/L	<.005	0.085	0.030	0.020	0.055	0.010
Cd	mg/L	<.005	0.045	0.050	0.050	0.050	0.030
Mn	mg/L	<.005	0.005	0.005	<.005	0.015	<.005
Co	mg/L	<.005	0.005	<.005	<.005	<.005	0.005
Cu	mg/L	0.020	0.090	0.010	<.005	<.005	<.005
Ag	mg/L	<.01	<.01	<.01	<.01	<.01	<.01
Fe	mg/L	0.06	1.44	0.04	0.02	0.04	0.05
Pb	mg/L	0.02	0.04	<.01	<.01	<.01	0.01
Cr	mg/L	<.005	0.110	<.005	<.005	<.005	<.005
Ni	mg/L	<.005	0.105	<.005	0.005	<.005	0.010

Operating Temperature = 25 deg. C
Operating Pressure = 400 psi (2850 KPa)

feed increased from 7.8 to 8.6 as it became more concentrated. The pH of the permeates remained close to 7.0. The detailed analysis of the permate showed that a very high quality permeate is generated by the TFC RO membrane. The concentrations of TOC and hardness in the permeate at a 30% volume reduction were 4.5 mg/L and 0.83 mg/L. The concentration of these components in the permeate at a 91% volume reduction decreased to 1 mg/L and 0.29 mg/L. The concentrations of other components in the permeates increased as they became more concentrated in the feed. The permeate at 91% volume reduction does, however, meet the requirements specified for the once through boiler systems. Conductivity, TDS, and dissolved silica in the permeates at 91% volume reduction were 27 microHmos/cm, 30 mg/L, and 2.85 mg/L respectively.

Infrared analysis of the RO permeate indicated a strong O-H stretch at 3750-3000 cm^{-1} but little evidence of a carbonyl stretch at 1700-1740 cm^{-1} or stretches at 1450, 1410 or 1370 associated with organic acids. Gas chromagraph analysis showed little sign of any organics in the sample.

The final salt water flux test showed a lower flux (0.87 m^3/m^2 D) than was observed during the initial salt test (2.27 - 1.22 m^3/m^2 D). The rejection of conductivity during this test was 97.4%. The flux rate during the test on UF permeate showed a sudden decrease after an 85% volume reduction (concentration factor of 6.67) had been obtained. The solubility of silica at 25°C at a pH of 8.6 is approximately 160 mg/L. It is believed that the decrease in flux at the end of the UF permeate test and the low salt water flux in the

final test is the result of silica precipitation plugging membrane pores.

The problems with silica precipitation can be decreased by increasing the operating temperature and increasing the pH of the feed. At a temperature of 40°C and a pH of 10 the solubility of silica is increased to over 560 mg/L. Figure 3-19 shows silica solubilities as a function of temperature and pH. To avoid precipitation of silica it is suggested that the concentration in the concentrate be limited to 80% of the maximum solubility. Operation at 40°C at pH 10 should allow concentration of the feed up to a concentration factor of seven (560 x 0.8 ÷ 63 = 7.1) or a percent volume reduction of 86% without problems of silica precipitation.

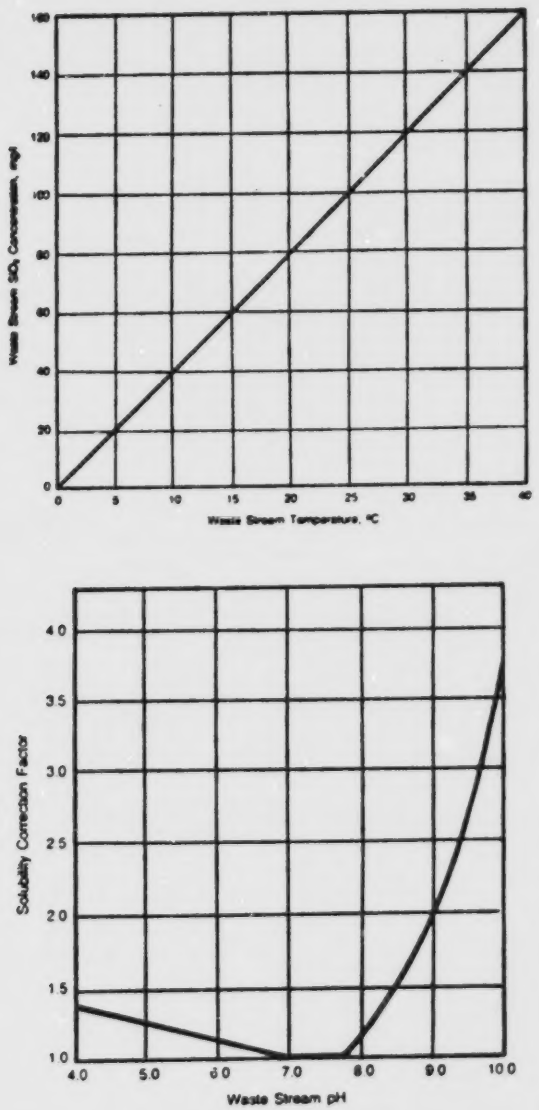
Barium and strontium sulfates may also be a source of scaling in RO systems. Special precautions to prevent scaling may be required when the feed concentrations of Ba or Sr are greater than 0.1 mg/L. The concentrations of these elements in the UF permeate and demulsified water are less than 0.1 mg/L but careful monitoring of different water sources should be conducted to insure that such scaling does not occur.

3.6.3 Reverse Osmosis Test on Demulsified Bitumen Emulsion

Flux rate data for the test of the TFC-RO membrane using demulsified filtered produced water as a feed are shown in Figure 3-20. Table 3-17 shows the results of analyses of the feed and of permeate samples taken during the run. Complete results including salt water flux test data are presented in Appendix F. The TFC-RO

FIGURE 3 - 19

SILICA SOLUBILITY AS A FUNCTION OF TEMPERATURE AND pH



from Rak (1984)

FIGURE 3 - 20

RO (DEMULSIFIED PRODUCED WATER)

TFC FLUX RATE VS VOLUME REDUCTION

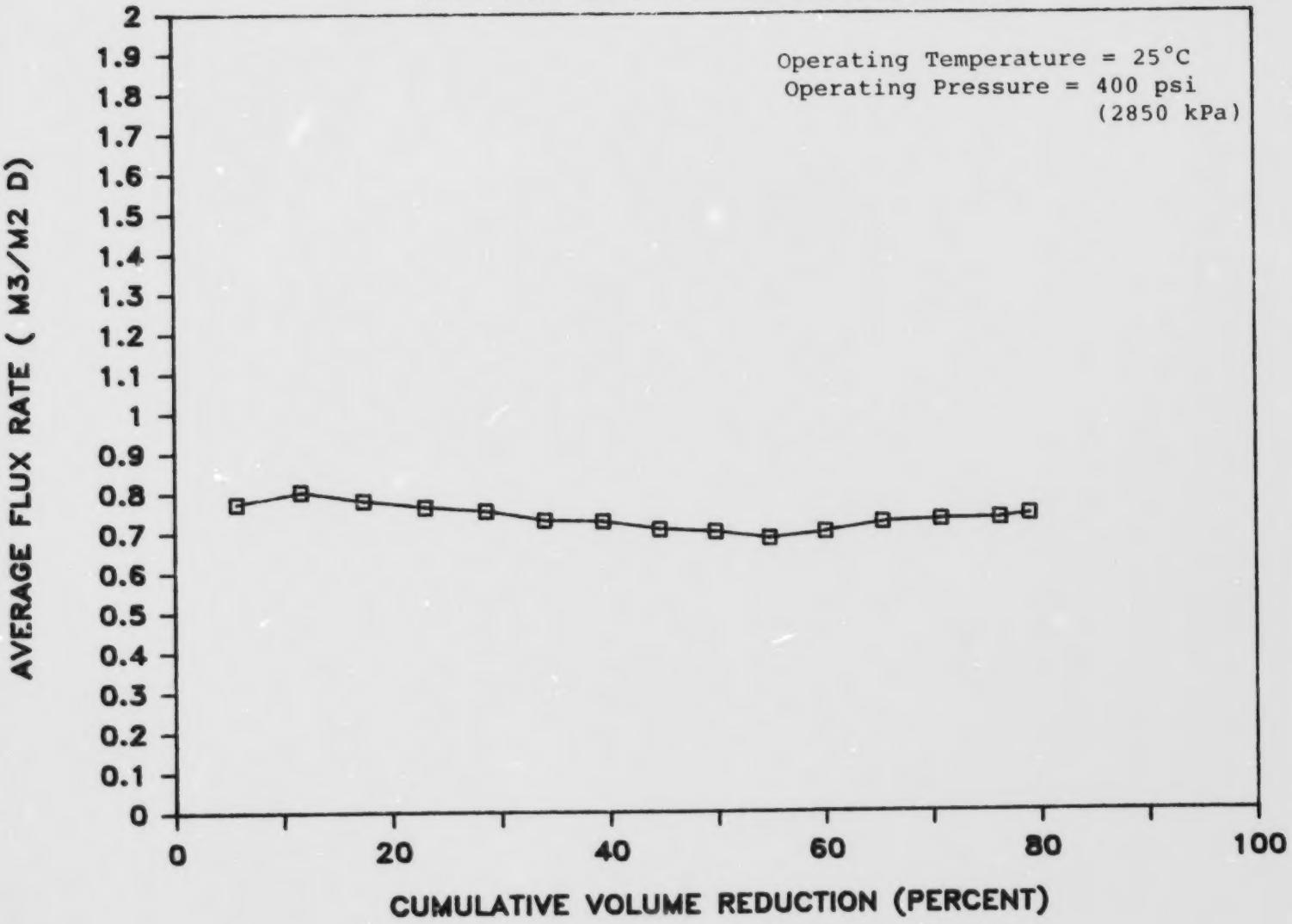


TABLE 3 - 17

ANALYTICAL DATA FOR RO TREATMENT OF
DEMULSIFIED PRODUCED WATER

PARAMETER	UNITS	CONCENTRATE FEED	CONCENTRATE FINAL	PERMEATE 30 MIN	PERMEATE 30%	PERMEATE 60%	PERMEATE 80%
pH		7.72	8.82	5.90	6.50	6.04	6.60
COND	uHmos/cm	980	4800	24	16.4	18.7	43.5
TURB	NTU	6.80	120.00	0.85	0.34	0.24	0.74
TOC	mg/L	135	600	2	3	4	15
TDS	mg/L	720	719	49	34	43	68
HARDNESS	mg/L	2.62	20.75	1.50	1.58	0.75	0.87
DIS SIO2	mg/L	59.60	330.30	0.70	0.70	0.90	1.50
F	mg/L	4.10	28.00	0.07	0.07	0.08	0.08
Cl	mg/L	192.0	1050.0	5.10	1.70	3.10	8.00
NO2	mg/L	<0.1	<5	<0.05	<0.05	<0.05	<0.05
PO4	mg/L	0.30	3.80	0.20	0.30	<0.2	0.20
NO3	mg/L	<0.2	0.20	<0.2	<0.2	<0.2	0.60
SO4	mg/L	78.00	480.00	0.50	0.20	0.20	<.2
Be	mg/L	<0.02	<0.02	<0.005	<0.005	<0.005	0.005
Mo	mg/L	0.040	0.260	<0.005	<0.005	<0.005	<0.005
Ca	mg/L	0.80	6.00	0.50	0.55	0.25	0.35
V	mg/L	<0.02	<0.02	<0.005	<0.005	<0.005	<0.005
Al	mg/L	0.09	0.30	0.05	0.13	0.04	0.09
Mg	mg/L	0.15	1.40	0.06	0.05	0.03	<0.01
Ba	mg/L	0.020	0.080	0.005	<0.005	0.010	<0.005
K	mg/L	6.20	37.00	0.11	0.02	0.05	0.11
Sr	mg/L	<0.02	0.060	<0.005	<0.005	<0.005	<0.005
Na	mg/L	210.0	1160.0	4.4	2.4	3.6	8.0
Zn	mg/L	0.020	0.330	0.030	0.015	0.045	<0.005
Cd	mg/L	<0.01	0.010	0.020	0.010	0.005	<0.005
Mn	mg/L	0.100	0.440	0.005	0.010	0.010	<0.005
Co	mg/L	<0.01	<0.01	<0.005	<0.005	<0.005	<0.005
Cu	mg/L	0.030	0.360	0.010	0.010	0.020	0.010
Ag	mg/L	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01
Fe	mg/L	0.83	2.90	0.10	0.05	0.22	0.03
Pb	mg/L	<0.03	<0.03	0.01	0.02	0.02	0.01
Cr	mg/L	<0.01	0.040	<0.005	<0.005	0.005	<0.005
Ni	mg/L	0.020	0.150	<0.005	0.005	<0.005	0.015

Operating Temperature = 25 deg. C
Operating Pressure = 400 psi (2850 KPa)

membrane used was a test membrane of the same type as was used for the UF permeate test.

Flux rates for the initial salt water flux test were stable and averaged 0.96 m^3/m^2 D. This is less than even the minimum flux observed during the initial salt water flux test for the UF permeate test which was 1.22 m^3/m^2 D. This lower flux may be due to inconsistencies in the membrane sheet or may be the result of a lower flowrate through the test unit. The percent rejection of conductivity during the test was 98.0%.

During the RO test using the demulsified produced water the flux rate remained stable near 0.74 m^3/m^2 D. This low flux rate is thought to be the result of the same factors which resulted in a lower initial salt water flux and the result of the slightly different feed water characteristics of the demulsified produced water. The run was stopped at an 80% volume reduction to avoid silica precipitation problems. The average rejection of conductivity during the run was 99.1%.

The detailed analyses of the feed water demonstrated that demulsified and filtered produced water has similar characteristics to TFC-UF permeate except that more oil is present in the demulsified water as shown by the higher turbidity. The demulsified water had a turbidity of 6.8 NTU, a TOC level of 135 mg/L, and an iron content of 0.83 mg/L. The UF permeate had turbidity of 0.75 NTU, TOC of 75 mg/L, and iron at 0.06 mg/L. The concentrations of other components in the demulsified water were very similar to those present in the UF permeate. The rejections of contaminants in this test were very similar to the rejections obtained for the previous RO test. The

permeate does still meet the quality criteria for the once through boiler system.

The flux rates during the final salt water test were stable at about 1.07 m^3/m^2 D, up slightly from the 0.96 m^3/m^2 D observed during the initial test. It is apparent that the silica scaling problem encountered in the previous run was not occurring during this test.

4.0 ECONOMIC ASSESSMENTS

4.1 Basis of Costing

Three separate processes for producing boiler feedwater from produced water have been outlined and estimates of capital and operating costs for each have been prepared. The processes involve:

i) using an ultrafiltration (UF) system followed by a softener,

ii) using a UF system followed by a reverse osmosis (RO) system, and

iii) using conventional technology for oil removal (induced gas floatation (IGF) and filtration) followed by RO.

The capacities of the processes are based on the same capacity system as was used by CH2M HILL in their 1982 Report, "Generation of Steam Using Low Grade Fuels and Field Produced Water for In-Situ Oil Recovery". The once through 80% boiler in the report was rated at 73 MW or 250 M BTU/h and required a feed of approximately 500,000 US gallons per day (USGPD). All processes have been designed to produce 500,000 US GPD of boiler feed water.

The designs of the steps used for pre and post membrane treatment were developed based on information available on present treatment practices from the literature and contacts with oil industry representatives.

The purchase costs for equipment other than the membrane process steps were based on estimates provided by equipment suppliers or from process equipment cost correlation tables. The total costs for process equipment were developed using factors of the purchase costs to estimate the other direct and indirect cost of installed

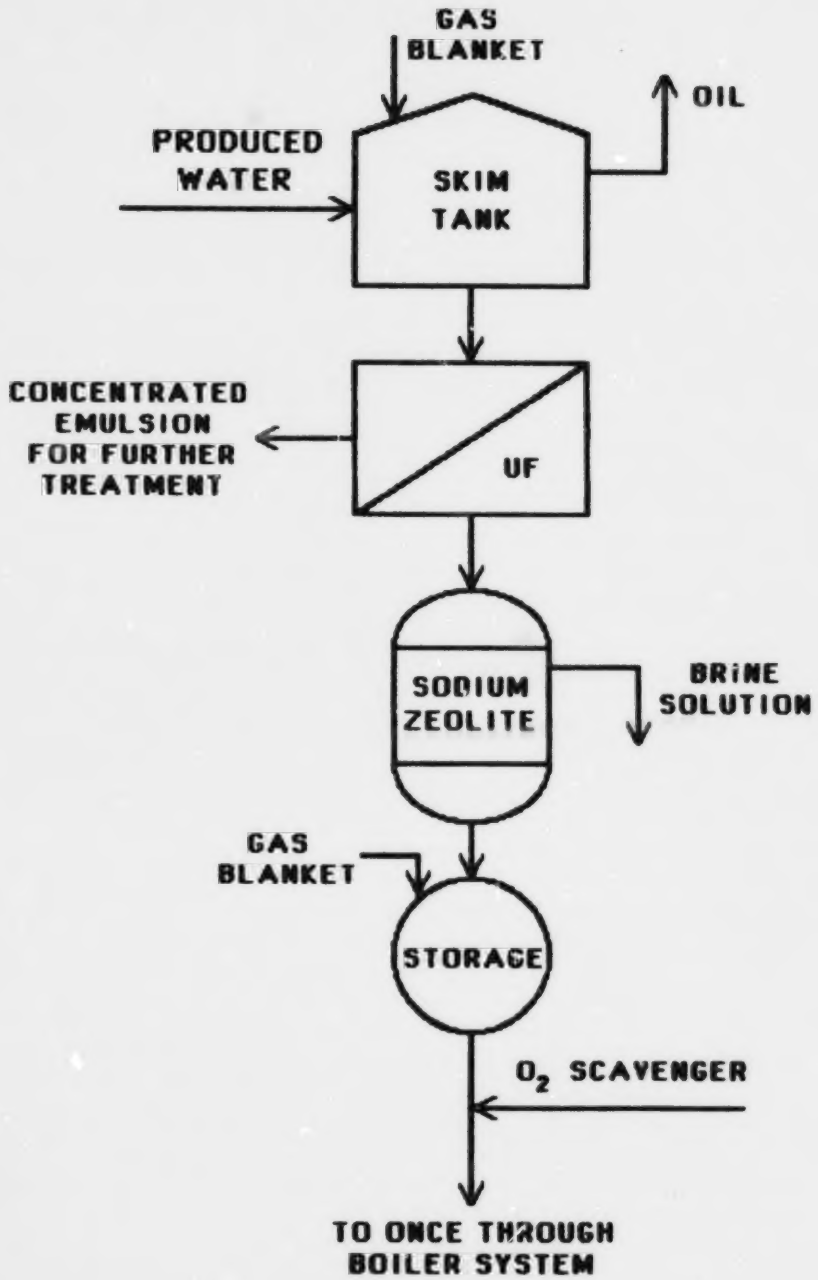
equipment. The installed costs include all costs associated with the facility including foundations, instruments, piping, insulation, buildings, and services, as well as construction and field expenses, engineering, and contractors fees. The costs for membrane systems presented in Appendix G are based on the results of experimental work and ZENON's up-to-date cost base information for membrane systems.

4.1.1 Ultrafiltration/Softening Process

Figure 4-1 shows a flow schematic for the ultrafiltration/softening (UF/SOFT) process for produced water treatment. The skim tank has been designed to have a two hour retention time and is equipped with a surface oil skimmer, a mechanism for bottom sludge removal, and a natural gas blanket. It is anticipated that this step will remove all free and suspended oil and produce an effluent containing approximately 1700 mg/L of emulsified oil.

Two ultrafiltration (UF) systems one using 8" spiral wrap membranes and the other using 1/2 inch tubular membranes were designed based on the results of experimental work and ZENON's experience at designing membrane systems. The design flux rates for the tubular system was estimated at 0.55 m^3/m^2 D. During the batch concentration run a flux of 0.62 m^3/m^2 D was obtained with the PS membrane at a volume reduction of 82% (CF of 5.6). Although the flux rates during the long term stability run at 90% volume reduction (CF of 10) were lower (0.47 m^3/m^2 D), it is reasonable to expect that by concentrating only to an 80% volume reduction (CF of 5) and optimizing the operating conditions a flux of 0.55 m^3/m^2 D can be maintained. ZENON's experience with tubular and spiral systems suggests that the flux

FIGURE 4 - 1
ULTRAFILTRATION/SOFTENING PROCESS
FOR PRODUCED WATER TREATMENT



rates which are obtained for spiral systems are generally 70% of those obtained with tubular systems. This lower flux is a result of somewhat poorer flow characteristics in the spiral systems. The design flux rate for the spiral UF system was 0.385 m^3/m^2 D. Both flux rates are considered to be conservative estimates and are toward the lower end of the range of acceptable flux rates for membrane systems. The system costs are virtually a direct function of the flux rate obtained therefore any increase in flux rate will reduce the system costs considerably.

The UF processes have been designed for 80% recovery of the feed. This recovery rate has been specified in order to maintain higher membrane flux rates and reduce fouling problems associated with very high rates of recovery. Based on the flux rate and permeate flow required detailed costing of the UF systems has been conducted. Appendix G presents a flow schematic and the purchase costs of the membrane systems.

The sodium zeolite softening system specified is a less expensive alternative to multi-step softening required in other produced water treatment processes. Such a system could be used since hardness and TDS levels in the UF permeate are expected to be low. The sodium zeolite system has been designed to reduce hardness levels to less than 0.5 mg/L.

A storage tank with a 24 hour nominal retention time has also been specified. Provisions have also been made for the addition of 50 mg/L of sodium sulfite as an oxygen scavenger.

4.1.2 Ultrafiltration/Reverse Osmosis Process

Figure 4-2 shows a flow schematic for the UF/RO process for produced water treatment. The skim tank and UF systems are identical to those in the process using UF/softening except that the UF system has a higher capacity to account for the loss of water in the RO concentrate.

The RO system was designed based on flux data generated during the experimental work. A spiral RO system was costed in detail using 8" diameter spiral modules with an 80% recovery rate to insure silica precipitation does not occur. The assumed flux rate based on the flux obtained at an 80% volume reduction during the RO test was 1 m^3/m^2 D.

Storage and oxygen scavenging were also specified in this flow sheet.

4.1.3 Induced Gas Floatation/Filtration/Reverse Osmosis Process

Figure 4.3 shows a flow schematic for the IGF/RO process for produced water treatment. The skim tank is designed based on a two hour retention time and as before is equipped with a surface skim and bottom sludge removal. Chemical demulsifier WITCO RTC 323 at 200 mg/L is added to the feed of the skim tank resulting in a much lower skim tank effluent oil concentration than with the previous systems. The skim tank is followed by a four chamber induced gas floatation unit, an intermediate storage tank, a sand filter, and cartridge filter. The cartridge filter is in place to protect the RO membrane from oil which may get through the sand filter during upset conditions.

FIGURE 4 - 2

ULTRAFILTRATION/REVERSE OSMOSIS PROCESS

FOR PRODUCED WATER TREATMENT

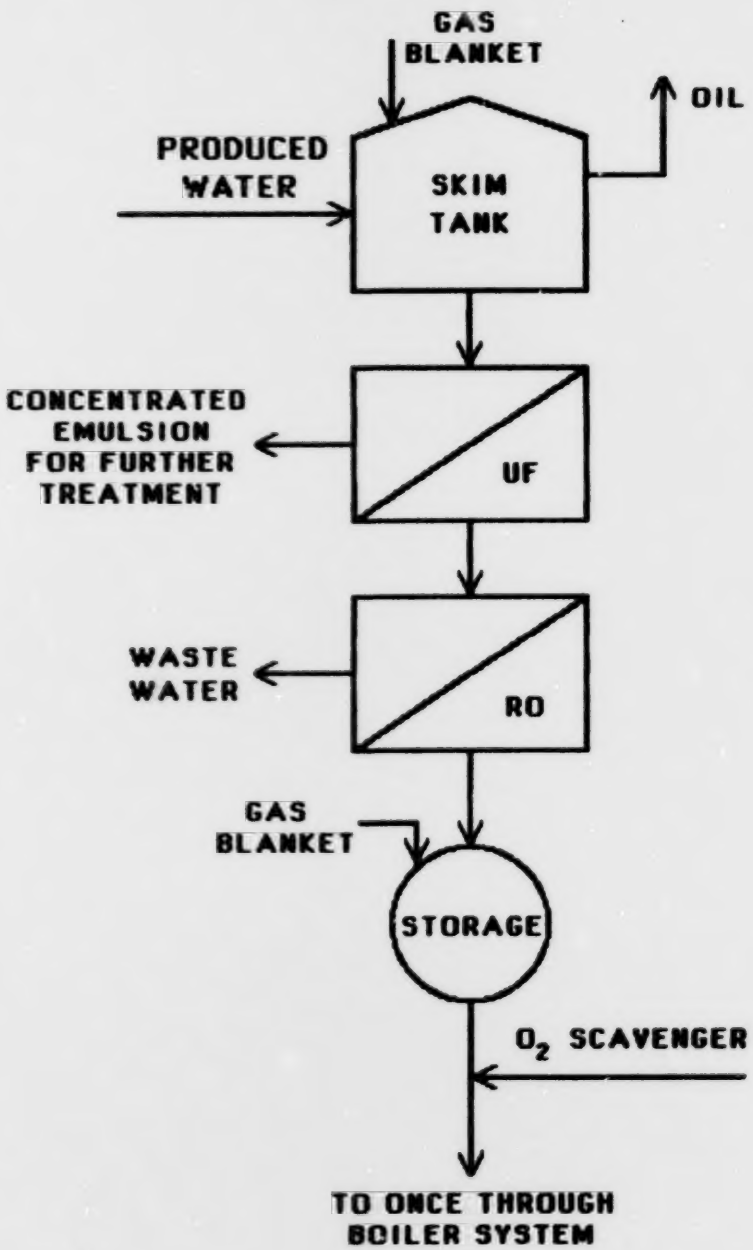
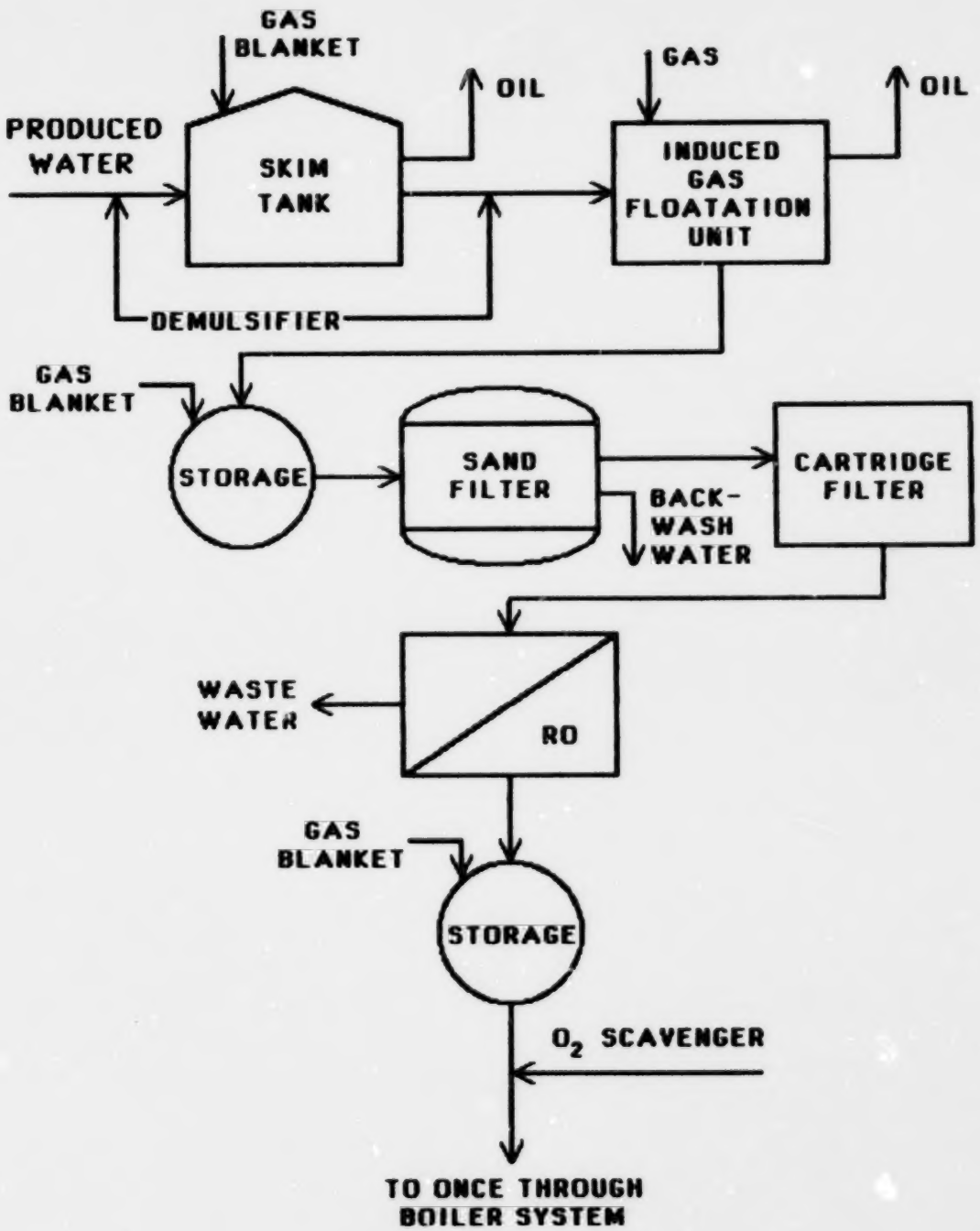


FIGURE 4 - 3

INDUCED GAS FLOATATION/FILTRATION/REVERSE OSMOSIS PROCESS

FOR PRODUCED WATER TREATMENT



The RO unit has been designed using 8" spiral membranes based on a flux rate of 0.775 m^3/m^2 D and 80% recovery of the feed. A tubular RO system was considered for this application but was felt to be both unnecessary and too expensive in comparison to the spiral membrane system.

Final storage and oxygen scavenging were also specified for this system.

4.2 Cost Estimates

Appendix G shows the details of the capital and operating costs for each step in the three processes for produced water treatment. Tables 4-1, 4-2, and 4-3 show summaries of these results for each of the three processes.

The total costs including amortization of capital at 13% over 10 years are very similar for the spiral UF/RO and IGF/RO processes. The costs for both processes are close to $7.00 per thousand gallons treated. The cost for the spiral UF/Softening process is only $4.84 per thousand gallons treated.

The sodium zeolite softening process specified in the UF/SOFT process is inexpensive relative to the softening required after conventional treatment of typical produced waters. The low hardness in the feed and reduction of TDS with the UF membrane allows for the much simpler sodium zeolite process to be used. The processes which had RO polishing are more expensive than the ones using only sodium zeolite softening but the quality of the effluent from the RO is much higher. The effluent from the RO exceeds the minimum criteria for the once through boiler feedwater quality considerably. This

TABLE 4 - 1

Total Costs for Ultrafiltration Process
for Produced Water Treatment

Capital Costs

	Spiral UF	Tubular UF
Pretreatment	$535,184	$535,184
UF System	$2,061,640	$8,888,799
Softening System	$205,120	$205,120
Storage & Oxygen Removal	$249,652	$249,652
Total Capital Costs	$3,051,596	$9,878,755
Amortized Capital Costs (over 10 years at 13% interest)	$561,494	$1,817,691

Operating and Maintenance Costs (per year)

	Spiral UF	Tubular UF
Pretreatment	$2,000	$2,000
UF System	$200,443	$692,594
Softening System	$25,475	$25,475
Storage & Oxygen Removal	$94,275	$94,275
Total Annual O & M Costs	$322,193	$814,344

Total Costs Including Capital Amortization

	Spiral UF	Tubular UF
Annual Costs	$883,687	$2,632,035
Cost Per Thousand Gallons Treated	$4.84	$14.42

TABLE 4 - 2

Total Costs for Ultrafiltration / Reverse Osmosis
Process for Produced Water Treatment

Capital Costs

	Spiral UF	Tubular UF
Pretreatment	$535,184	$535,184
UF System	$2,612,996	$11,040,414
RO System	$995,918	$995,918
Storage & Oxygen Removal	$249,652	$249,652
Total Capital Costs	$4,393,750	$12,821,168
Amortized Capital Costs (over 10 years at 13% interest)	$808,450	$2,359,095

Operating and Maintenance Costs (per year)

	Spiral UF	Tubular UF
Pretreatment	$2,000	$2,000
UF System	$248,698	$880,472
RO System	$115,515	$115,515
Storage & Oxygen Removal	$94,275	$94,275
Total Annual O & M Costs	$460,488	$1,092,262

Total Costs Including Capital Amortization

	Spiral UF	Tubular UF
Annual Costs	$1,268,938	$3,451,357
Cost Per Thousand Gallons Treated	$6.95	$18.91

TABLE 4 - 3

Total Costs for Induced Gas Floatation / Reverse Osmosis Process for Produced Water Treatment

Capital Costs	
Pretreatment	$1,464,897
RO System	$1,112,777
Storage & Oxygen Removal	$249,652
Total Capital Costs	$2,827,326
Amortized Capital Costs (over 10 years at 13% interest)	$520,228
Operating and Maintenance Costs (per year)	
Pretreatment	$551,230
RO System	$123,523
Storage & Oxygen Removal	$94,275
Total Annual O & M Costs	$769,028
Total Costs Including Capital Amortization	
Annual Costs	$1,289,256
Cost Per Thousand Gallons Treated	$7.06

higher than minimum quality feedwater may have an effect in reducing operating and maintenance costs in the boiler. The RO effluent is so clean in fact that it may also be worth considering further deionization treatment and use in utility boilers. The RO treatment also has the ability to remove higher levels of hardness present in many produced waters.

Figure 4-4 shows the yearly amortized capital and operating costs for the three processes. Spiral UF systems have been used in the two processes employing UF. The total costs for the spiral UF/RO and IGF/RO are similar but the UF/RO has a larger proportion (64%) of capital cost than the IGF/RO processes (40%). The UF membrane process has a higher capital cost but much lower operating costs than conventional IGF treatment. The UF/SOFT process is less expensive overall but the quality of the effluent is lower than from the RO processes.

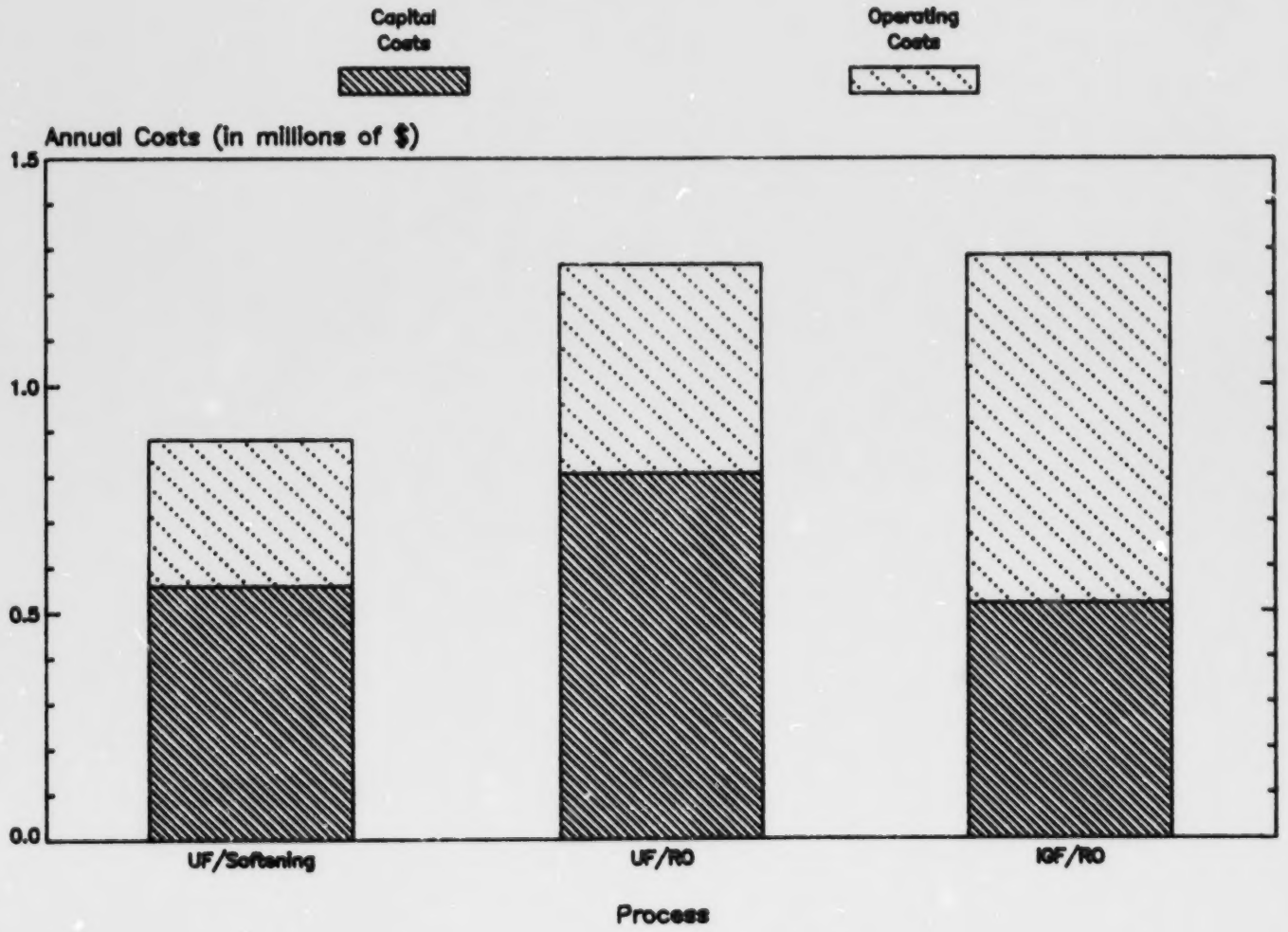
If the cost of the RO pretreatment by IGF and filtration is combined with the sodium zeolite softening the total capital cost is $1,919,669 and the operating costs are $670,980 to give a cost per thousand gallons treated of $5.61. This is more expensive than the UF/SOFT process but less than for the UF/RO and IFG/RO processes. The comparison demonstrates that the spiral UF process can be more economical than conventional treatment processes.

In their 1982 report, CH2M Hill specified a skim tank with demulsifier addition followed by IGF for produced water treatment prior to a thermosludge steam injection process. The capital and operating costs for this two stage process were $880,000 and $300,000/year in 1982. The capital and operating cost for the skim

FIGURE 4 - 4

Amortized Capital and Operating Costs

for Different Processes for Treating Produced Water



tank with demulsifier addition followed by IGF, sand filtration, and a cartridge filter estimated in this work are $1,465,000 and $551,230/year respectively. The differences in costs represent the additional cost of intermediate storage and sand and cartridge filtration.

The CH2M Hill report also estimated the capital and operating costs for a complete treatment process to produce once through boiler feed from produced water at $6,880,000 and $985,000/year respectively. If this capital cost in amortized over 10 years at 13% interest, and added to the operating costs, the cost per thousand gallons treated becomes $12.33. This is higher than the estimates for complete systems developed in this study, but the CH2M Hill study assumed a feedwater with a considerably higher level of hardness (over 130 mg/L) and TDS (800 - 20,000 mg/L). This harder water requires a hot lime softening step and a multi-stage ion exchange for deionization of the water. These operations add considerable expense to the overall process. RO system costs for treatment of very hard water could be higher than for the RO systems considered in this study. Extra expense might be required to prevent scaling of Ca and Mg with some very hard waters.

The comparison with CH2M Hill does, however, suggest the costs of treatment using membranes is competative with conventional processes.

The costs of the tubular systems are very high relative to the spiral systems but the costs are a direct function of the flux rate which can be maintained in the system. Flux data used for estimating the size of systems required were based on flux rates in

NRC flat sheet test cells. The flux rates in actual tubular systems may be considerably higher than obtained in the test cells. Tubular systems also have the advantage that mechanical cleaning of membrane surfaces can be carried out. This cleaning may be required to maintain higher more economical flux rates.

5.0 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

5.1 Conclusions

- The technical feasibility of using UF membranes for removing bitumen from a produced water emulsion has been demonstrated.
- Emulsion characterization work demonstrated the considerable variability in produced water and the very stable nature of the emulsion. The sample obtained had oil levels typical of higher oil produced waters (1700 mg/L) and an unusually low hardness (4 mg/L). Detailed chemical analysis showed the presence of about 60 mg/L of naphthenic acid which is though to be an important factor in maintaining emulsion stability.
- Screening tests identified three membranes as being most appropriate for this application. The thin film composite (TFC) UF memorane G10 consistently produced the highest quality permeate and maintained a very stable flux rate. The CHP and polysulfone (PS) E500 membranes produced similar quality permeates and maintained high and reasonably stable flux rates.
- As expected during the screening tests the flux rates for all membranes improved as the temperature of operation was increased. There also appeared to be a trend for increasing flux rates at higher pH.
- During the batch concentration test it was demonstrated that flux rates can be relatively stable even at a 5 fold concentration of the raw emulsion.

- The concentrated emulsion remained stable at a 90% volume reduction or at a concentration factor of 10.
- The long term stability run demonstrated that there is no deterioration in permeate quality with time for any of the membranes tested. This run also demonstrated that effective membrane cleaning will be critical to the economic viability of the process.
- The reverse osmosis tests demonstrated that RO treatment is a simple and effective method of producing boiler feedwater from produced water from which oil has been removed. Silica solubitity problems limit the possible recovery to 80-85% for a 60 mg/L dissolved silica feed.
- Based on the estimated flux rates predicted from experimental data the economics of spiral UF membrane systems are competative with conventional treatment processes. Tubular systems will be uneconomical unless the flux rates for such systems can be increased.
- Simple sodium zeolite softening for treatment of low hardness feeds is less expensive than reverse osmosis but the RO is capable of handling higher hardness feeds and producing higher quality effluents.

5.2 Recommendations

The membrane configurations used during all testing to date have been flat sheet NRC test cells or a large plate and frame test unit. If a commercial scale membrane system is to be put in place it will require the use of configured membrane units probably tubular,

spiral wrap, or hollow fiber. The flow characterics in these systems will have a major impact on the flux rates which can be maintained and the efficiency of membrane cleaning. Work should be conducted using a variety of membrane configurations similar to individual modules of large systems but on a small scale. The cost of the tubular system described in this work was considerably higher than that of the spiral system but work with small scale tubular systems may show significantly higher fluxes and better cleanability than other systems. Since large systems usually consist of many modules it is possible to test a single module unit and generate data which can be used to accurately predict the performance of large systems. Such testing should be conducted to generate accurate data on flux rates, membrane fouling, and cleaning efficiency for predicting the performance of full scale systems. Economic assessments of membrane systems can be more accurately refined based on this data.

The choice of membranes from the prescreening tests were made based on flux rates, clarity of permeate, and rejection of TOC. In this application it may in fact be desirable to have a very loose membrane with poor rejection of TOC in order that the surfactant material stabilizing the emulsion passes through the membrane and allows the emulsion to break spontaneously. The emulsion could be concentrated using such a loose membrane to see if spontaneous emulsion breaking will take place.

In addition the effects of produced water aging on membrane system operation should be considered. Once laboratory work on small scale configured systems has demonstrated that stable high flux rates can be obtained and that effective cleaning procedures can be

developed, the small scale configured systems should be tested at field locations using fresh emulsions.

Further work should also include exploration of the upper temperature limits of membrane system operation to determine exactly what temperatures can be used and what benefits are achieved by this higher temperature operation.

In this work only one sample of emulsion with an oil level of 1700 mg/L from Texaco's Fort McMurry operation was tested. It is known that there is considerable variability in the emulsions from a single source and even more variability between different sources. As well there are a number different stages of conventional treatment after which membrane systems may be applied. Potential sources of water suitable for UF treatment which should be considered are, skim tank effluent (1000-2000 ppm oil), high temperature separator (HTS) effluent (100-500 ppm oil), and induced gas floatation (IGF) effluent (10-40 ppm oil). Samples of these emulsions should be obtained from different sources to assess the general application of the technology. Flux rates for lower oil content emulsions may be higher than for the emulsion tested in this work resulting in lower capital and operating costs for these membranes systems. Potential sources of water suitable for RO treatment include UF permeates and filtered IGF effluents.

6.0 REFERENCES

CH_2M HILL (1982). "Generation of Steam Using Low Grade Fuels and Field Produced Water for In-Situ Oil Recovery", Report Prepared for Energy, Mines, and Resources, Canada.

Rak, S.F. (1984). "Reverse Osmosis Membrane Fouling and Pretreatment Considerations", Industrial Water Engineering, Vol. 21, No.4, 12-15.

AWWA, APHA, & WPCF (1971). Standard Methods for the Examination of Water and Wastewater, 13 ed.